

**O‘ZBEKISTON RESPUBLIKASI OLIY VA O‘RTA
MAXSUS TA‘LIM VAZIRLIGI**

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FIZIKAVIY KIMYODAN MASALALAR TO‘PLAMI

*Oliy o‘quv yurtlarining 520000-muhandislik ishi hamda 540000-ishlab
chiqarish va qayta ishlash tarmoqlari ixtisosliklarida tahsil oluvchi
talabalari uchun o‘quv qo‘llanma sifatida tavsiya etilgan*

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O'quv qo'llanmada fizikaviy kimyo fanining barcha nazariy bo'limlariga tegishli bo'lgan masalalar tanlab olingan. Har bir bo'lim qismlarining nazariy asoslariga oid qonun, tushuncha, ta'rif va boshqalardan so'ng shularga tegishli masalalarni yechishga doir misol hamda masalalar keltirilgan. Talabalar fizikaviy kimyo fanining materiallarini yanada mukammal va chuqurroq tushunishlari, mustaqil ravishda tahlil qilib ta'lim olishlari uchun ko'p variantli masalalar ham berilgan.

Mazkur o'quv qo'llanma fizikaviy kimyo kursidan masalalar yechishda dasturilamaldir. Unda har bir bob bo'yicha nazariy ma'lumotlar tushunarli tarzda bayon qilingan. Shuningdek, o'quv qo'llanmada masalalarni yechish tartibi va hisoblash usullari ham keltirilgan.

Ushbu kitob oliy o'quv yurtlarining fizikaviy kimyo fani dasturi asosida ta'lim olayotgan talabalari uchun mo'ljallangan.

SO‘ZBOSHI

Fizikaviy kimyo fani kimyoviy jarayonlarni har taraflama atroflicha o‘rganish, kimyoviy jarayonlarni ongli ravishda idora qilish, ya’ni jarayonlarni olib borishda optimal sharoitni belgilashga imkon yaratadi.

Shu bilan birga, bu fandagi mavhum nazariyalar va kattaliklarning asl ma’nosini tushunish va anglashda, chiqarilgan xulosalarning amaliy ahamiyatini tushunishda va amalda qo‘llashda fizikaviy kimyo masalalarini yechish alohida o‘rin tutadi va boshqa kimyo fanlariga nisbatan ham katta ahamiyatga ega.

Fizikaviy kimyo fani kimyo fanlarining hamma bo‘limlarini umumlashtiruvchi, universal qonunlar beruvchi nazariy fandir.

Fizikaviy kimyo fani, asosan, kimyoviy jarayonlarning quyidagi muhim muammolarini o‘rganadi:

1. Kimyoviy jarayonning yo‘nalishini, ya’ni ma’lum moddalar o‘rtasida kimyoviy reaksiyalarning sodir bo‘lishi yoki bo‘lmashligini aniqlash. Reaksiyalar qanday sharoitlarda amalga oshadi, jumladan, reaksiya chap tomondan (mahsulotlar hosil bo‘lish tomoniga) o‘ngga yoki aksincha, o‘ngdan chapga (dastlabki moddalar hosil bo‘lish tomoniga) boradimi?

a) reaksiya bir vaqtning o‘zida ikki tomonga qaytar ravishda sodir bo‘ladimi?

b) agar reaksiya qaytar bo‘lsa, unumi qanday bo‘ladi va reaksiya unumi miqdori past bo‘lsa, uni oshirishning yo‘llarini belgilaydi. Bu masalalarni tajribalar o‘tkazmasdan turib, fizikaviy kimyoning katta yutug‘i bo‘lgan aniqlashning nazariy hisoblash usullarini qo‘llashni o‘rganadi.

2. Reaksiyalar natijasida ko‘pincha faza (soha)lar soni o‘zgaradi yoki yangi fazalar (cho‘kma, gaz, suyuq holatda) hosil bo‘ladi. Fizikaviy kimyo jarayonda ishtirok etayotgan moddalarning shu fazalar bo‘yicha taqsimlanishi, o‘zgarishi va boshqa holatlarini o‘rganadi.

3. Kimyoviy jarayon natijasida issiqlik ajralishi (yoki yutilishi), elektr energiya vujudga kelishi, nurlanish, portlashlar sodir bo‘lishi, ya’ni kimyoviy energiyaning boshqa energiyalar turiga aylanishi va aksincha, turli energiyalar kimyoviy energiyaga aylanishi mumkin. Demak, kimyoviy jarayonlar bilan birgalikda fizikaviy o‘zgarishlar (energiya fizika obyekti bo‘lib hisoblanadi) yonma-yon sodir bo‘ladi. Fizikaviy kimyo jarayonlarning bu ikki xil tomonini e’tiborga olib, ularni o‘zaro bog‘lagan holda o‘rganadi.

4. Har qanday jarayon ma’lum tezliklarda boradi. Fizikaviy kimyo fani kimyoviy jarayonlarning tezligiga turli omillarning (parametr) ta’sirini o‘rganish natijasida reaksiyaning yo‘nalishini tezlatish hamda kerak bo‘lmagan yo‘nalish tezligini kamaytirish usullarini o‘rganadi.

5. Reaksiyalarning borish mexanizmini, ya’ni qanday yo‘llar bilan sodir bo‘lishini o‘rganadi. Ba’zan reaksiya mahsuloti olingan dastlabki moddalarning bevosita ta’siri natijasida to‘g‘ridan-to‘g‘ri hosil bo‘ladi. Ayrim hollarda kimyoviy jarayon bosqichma-bosqich, oraliq moddalar hosil bo‘lishi bilan boradi. Masalan, $H_2 + Cl_2 \rightarrow 2HCl$; $H_2 + 0,5O_2 = H_2O$. Oraliq moddalar hosil bo‘lishi sababli bu reaksiyalar ancha murakkab tarzda sodir bo‘ladi.

6. Moddalarning kimyoviy reaksiyalarga kirishish qobiliyati va boshqa holatlari ularning tuzilishiga bog‘liq ravishda ro‘y berishi va bunda sodir bo‘ladigan qator hodisalarni tushuntirib beradi.

Yuqorida bayon etilganlarni va o‘zbek tilida zamon talablariga javob beruvchi bunday to‘plamning yo‘qligini hisobga olgan holda ushbu o‘quv adabiyoti yaratildi. Uni yaratishda mualliflar o‘zlarining Toshkent kimyo-texnologiya institutining tegishli kafedralarida ko‘p yillar davomida talabalarga bergan ma’ruzalarini asos qilib olishgan. Kitobning «Elektr yurituvchi kuch» va

«Kimyoviy muvozanat» boblari dotsent B. H. Hasanov, «Termokimyo», «Eritmalar», «Elektrolit eritmalar» va «Elektr o'tkazuvchanlik», «Elektrokimyoviy reaksiyalar kinetikasi», «Elektroliz» boblari dotsent Sh. P. Nurullayev, so'zboshi va qolgan boblar O'zR FA akademigi, professor H. R. Rustamov tomonidan yozilgan.

Kitob ayrim kamchiliklardan xoli bo'lmasligi mumkin, albatta. Shuning uchun o'quv qo'llanma haqidagi fikr va mulohazalarni mualliflar minnatdorchilik bilan qabul qiladilar.

BA'ZI FIZIKAVIY VA KIMYOVIY KATTALIKLARNING QIYMATI

Avogadro soni	$N = 6,0229 \cdot 10^{23} \text{ mol}^{-1}$
Faradey soni	$F = 96490 \text{ k/g-ckv}$
Plank doimiysi	$h = 6,6252 \cdot 10^{-34} \text{ J} \cdot \text{sek}$
Bolsman doimiysi	$k = 13,803 \cdot 10^{-22} \text{ J/grad}$
Universal gaz doimiysi	$R = 8,3143 \text{ J/mol} \cdot \text{grad} =$ $= 0,082057 \text{ atm/mol} \cdot \text{grad} =$ $= 8,3143 \cdot 10^7 \text{ erg/mol} \cdot \text{grad}$
Proton massasi	$m_p = 1,67239 \cdot 10^{-27} \text{ kg}$
Neytron massasi	$m_n = 1,67470 \cdot 10^{-27} \text{ kg}$

Amalda qo'llanilib kelinayotgan kattaliklarni SI sistemasiga o'tkazish uchun koeffitsiyentlar quyidagi jadvalda berilgan:

Isho- rasi	Kattaliklar nomi	SI sistemasidagi o 'lchov birligi	1963-yilgacha qo'llangan sistemadagi o'lchov birligi	SI sistemasiga o'tkazish koeffitsiyenti
1	2	3	4	5
<i>A</i>	Sistemaning bajargan ishi	J/kmol	l · atm/mol kkal/mol	$1,0133 \cdot 10^5$ $4,187 \cdot 10^6$
<i>C</i>	Issiqlik · sig'imi	J/kmol · grad	kal/mol · grad	$4,187 \cdot 10^3$
<i>d</i>	Zichlik	kg/m ³	g/sm ³	10^3
<i>E</i>	Energiya	J	erg	10^{-7}
<i>F</i>	Gelmgols funktsiyasi	J/kmol	kkal/mol	$4,187 \cdot 10^6$
<i>G</i>	Gibbs funksiyasi	J/kmol	kkal/mol	$4,187 \cdot 10^6$
<i>F</i>	Kuch	N	din	10^{-5}
<i>H</i>	Entalpiya	J/kmol	kkal/mol	$4,187 \cdot 10^6$
<i>m</i>	Massa	kg	g	10^{-3}
<i>K</i>	Krioskopik konstanta	grad · 10 ³ kg/kmol	grad · g/mol	1

I bob

TERMODINAMIKANING BIRINCHI QONUNI

Termodinamikaning I (bosh) qonuni umumiy qonun bo'lib, energiyaning saqlanish qonunini miqdoriy ifodalaydi, ya'ni turli energiyalar o'rtasidagi miqdoriy nisbatni o'rganadi. Birinchi qonun bo'yicha jarayonning borish sharoitiga, unda qanday moddalar ishtirok etganligiga qaramasdan, doimo energiya bir turining ma'lum miqdori ma'lum miqdordagi boshqa turga aylanadi (*ekvivalentlik*, ya'ni *barobarlik qonuni*).

Kimyoviy termodinamika umumiy termodinamikaning bir bo'limi bo'lib, unda umumiy termodinamikaning hamma qonun va tenglamalari, jumladan, ekvivalentlik qonuni o'z kuchini saqlaydi. Kimyoviy reaksiyalarda issiqlik ajraladi yoki yutiladi, elektr energiya vujudga keladi va hokazo, ya'ni kimyoviy energiya boshqa turdagi energiyaga aylanadi. Kimyoviy termodinamika kimyoviy energiya bilan energiyaning boshqa turlari o'rtasidagi miqdoriy nisbatni o'rganadi.

Kimyoviy energiya — ichki energiya deb atalgan energiyaning kimyoviy jarayonda qanchagacha o'zgargani (ko'paygani yoki kamaygani)ga teng. Ichki energiya sistemani tashkil qilgan hamma tarkibiy bo'laklarning bir-biriga o'zaro ta'siri potensial energiyasi bilan ularning kinetik energiyasi yig'indisiga teng. Ichki energiyaning (U) mutlaq (absolut) miqdorini o'lchay olmaymiz, lekin jarayonda qanchaga o'zgarganligini bilvosita usullar bilan aniqlash mumkin:

$$\Delta U = U_2 - U_1. \quad (1.1)$$

Birinchi bosh qonunning matematik ifodasi quyidagicha:

$$\delta Q = dU + \delta A, \quad (I.2)$$

bunda: Q — issiqlik; U — ichki energiya; A — ish.

Demak, sistemaga berilgan issiqlik sistemaning ichki energiyasini orttirishga va foydali ish bajarishga sarf bo‘ladi. Agar biror kattalikning kimyoviy jarayonda o‘zgarishi faqat sistemaning boshlang‘ich va oxirgi holatiga bog‘liq bo‘lsa, bu xil kattalik to‘liq funksiya deyiladi va uning cheksiz kichik miqdori d harfi bilan ifodalanadi. To‘liq funksiya ifodasini integrallash mumkin. Agar funksiyaning jarayonda o‘zgarishi sistemaning boshlang‘ich va oxirgi holatidan tashqari yana sistemaning o‘tish yo‘liga bog‘liq bo‘lsa, bunga noto‘liq funksiya deyiladi va uning cheksiz kichik miqdori δ harfi bilan ifodalanadi. Noto‘liq funksiyaning umumiy ko‘rinishda integrallash mumkin emas. Agar o‘tish yo‘li ma’lum bo‘lsagina integrallash mumkin.

Ichki energiya to‘liq funksiya bo‘lib, issiqlik va ish noto‘liq funksiyalardir.

Agar foydali ish gazning faqat kengayib bajargan ishidan iborat bo‘lsa,

$$\delta A = p dV \text{ va } A = \int_1^2 p dV. \quad (I.3)$$

Agar uni asosiy tenglamaga qo‘ysak,

$$\delta Q = dU + p dV. \quad (I.4)$$

Izoxorik (turg‘un hajmda boradigan) jarayonlarda sistemaning

holatini belgilovchi ichki energiya (U) bo'lsa, izobarik (o'zgarmas bosimda boradigan) jarayonlarda — entalpiya (H) bo'ladi.

ISSIQLIK SIG'IMI

Fizikaviy kimyoda atom, molar va solishtirma issiqlik sig'irlari tushunchasi mavjud. Bu issiqlik sig'irlarining o'lchami quyidagicha:

solishtirma c — $J/g \cdot \text{grad}$, molar c — $J/mol \cdot \text{grad}$ yoki J (Joul) o'rnida kaloriya bo'lishi mumkin.

Izoxorik ($V = \text{const}$) boradigan jarayonlar uchun molar izoxorik issiqlik sig'imi C_v va izobarik jarayonlar uchun molar izobarik issiqlik sig'imi C_p ifodalari mavjud. Ular orasida quyidagi bog'lanish bor:

$$C_p - C_v = R. \quad (1.5)$$

Issiqlik sig'imi haroratga bog'liq bo'lganligidan o'rtacha ($\bar{c}$) va chin (C) issiqlik sig'imi ifodalari mavjud.

O'rtacha issiqlik sig'imi ($\bar{c}$) massa birligidagi modda T_1 dan T_2 gacha isitilganda sarflangan issiqlikning (Q) harorat o'zgarishi nisbatiga teng:

$$\bar{c} = \frac{Q}{m(T_2 - T_1)}, \quad Q = \bar{c}m(T_2 - T_1). \quad (1.6)$$

Mazkur massa birligidagi modda haroratini cheksiz kichik miqdorda oshirish uchun sarflangan issiqlik chin issiqlik sig'imi (C) bo'ladi:

$$C = \frac{\delta Q}{m dT}; \quad Q = m \int_{T_1}^{T_2} C dt. \quad (1.7)$$

Bu ikki tenglamadan:

$$\bar{c}(T_2 - T_1) = \int_{T_1}^{T_2} c dT.$$

Demak, C dan $\bar{c}$ ga o'tish:

$$\bar{c} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C dT. \quad (1.8)$$

$\bar{c}$ dan C ga o'tish:

$$C = \frac{d[\bar{c}(T_2 - T_1)]}{dT}. \quad (1.9)$$

Amaliy hisoblar uchun issiqlik sig'iminining haroratga bog'liq holda o'zgarishi empirik tenglama bilan ifodalanadi:

$$\left. \begin{aligned} C &= a + bT + cT^2 + dT^3 \\ C &= a + bT - c'T^{-2} \end{aligned} \right\} \quad (1.10)$$

a, b, c, c', d — koeffitsiyentlarning qiymatlari turli moddalar uchun ma'lumotnomalarda berilgan.

Ichki energiya va entalpiya, ularning o'zgarishi quyidagi tenglamalardan topilishi mumkin:

$$\left. \begin{aligned} dU &= C_v dT; \quad \Delta U = \int_{T_1}^{T_2} C_p dT \\ dH &= C_p dT; \quad \Delta H = \int_{T_1}^{T_2} C_p dT \\ H &= U + PV; \quad dH = dU + d(PV) \\ \text{Ideal gazlar uchun:} \\ \Delta H &= \Delta U + \Delta n RT, \text{ bunda } \Delta n = \sum n_i, M - \sum n_i, d \end{aligned} \right\} \quad (1.11)$$

n_M, n_d — mahsulot va dastlabki gazsimon moddalarning mol soni.

Kimyoviy jarayonlarda ajraladigan yoki yutiladigan issiqlik *reaksiyaning issiqlik effekti* deyiladi.

Izoxorik jarayonda ($V = \text{const}$) sistemaga berilgan yoki yutilgan issiqlik izoxorik issiqlik effektidir (Q_v):

$$\Delta Q_v = \Delta U. \quad (1.12)$$

Izobarik jarayonda ($p = \text{const}$) issiqlik effekti:

$$Q_p = \Delta H. \quad (1.13)$$

Quyidagi jadvalda turli jarayonlarda ideal gazlar uchun issiqlik va ish ifodasi berilgan.

Jarayon	Ish	Issiqlik	Holat tenglamasi
izotermik	$2,3n \lg \frac{V_2}{V_1}$	$2,3nRT \lg \frac{p_1}{p_2}$	$pV = \text{const}$
izoxorik	0	$nC_v(T_2 - T_1)$	$\frac{p}{T} = \text{const}$
izobarik	$p(V_2 - V_1)$	$nC_p(T_2 - T_1)$	$pV^\gamma = \text{const}$
adiabatik	$nC_v(T_2 - T_1)$	0	$Tp^{\frac{\gamma-1}{\gamma}} = \text{const}$

Bu yerda: $\gamma = \frac{C_p}{C_v}$; n — mol soni; C_v , C_p — izoxorik va izobarik molar issiqlik sig'implari.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. 200—300 K oralig'ida ammiak NH_3 ning izobarik (chin) issiqlik sig'imi haroratga quyidagicha bog'liq:

$$C_p = 24,8 + 37,5 \cdot 10^{-3} T - 7,36 \cdot 10^{-6} T^2 \text{ J/mol} \cdot \text{grad}.$$

200—300 K oralig'ida NH_3 ning o'rtacha molar izobarik issiqlik sig'imini aniqlang.

Yechish. (I. 8) va (I. 10) tenglamalardan:

$$\begin{aligned} \bar{c} &= \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_p dT = \frac{1}{300 - 200} \int_{200}^{300} (24,8 + 37,5 \cdot 10^{-3} T - 7,36 \cdot 10^{-6} T^2) \times \\ &\times dT = 24,8 + \frac{1}{2} (3_{300} + 2_{200}) 37,5 \cdot 10^{-3} - \frac{1}{3} (3_{200}^2 + 3_{300} \cdot 2_{200}) \cdot 7,36 \cdot 10^{-6} = \\ &= 33,7 \text{ J/mol} \cdot \text{grad}. \end{aligned}$$

2. Titan oksid (TiO_2) ning o'rtacha solishtirma issiqlik sig'imi 0° dan $t^\circ \text{C}$ gacha quyidagicha o'zgaradi:

$$\bar{c}_p = 0,782 + 1,41 \cdot 10^{-4} t - 0,557 \cdot 10^{-3} t^2 \text{ J/g} \cdot \text{grad}.$$

500°C dagi chin issiqlik sig'imini aniqlang.

Yechish. (I. 9) va (I. 10) tenglamalar yordamida yechiladi:

$$\begin{aligned} \bar{c} &= \frac{d[\bar{c}(T_2 - T_1)]}{dT} = \frac{d(\bar{c}t_2)}{dt} = 0,782t_2 + 1,41 \cdot 10^{-4} t_2^2 - 0,557 \cdot 10^{-3} t_2^2 = \\ &= 0,782 \cdot 500 + 2 \cdot 1,41 \cdot 10^{-4} \cdot 500^2 + 0,557 \cdot 10^{-3} \cdot 500^2 = 0,883 \text{ J/g} \cdot \text{grad}. \end{aligned}$$

3. 100 g CO_2 gazi 0° harorat va $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda turibdi. Quyidagi jarayonlarda:

- gaz izotermik ravishda $V = 0,2 \text{ m}^3$ gacha kengayganda;
- shu hajmga izobarik ravishda kengayganda;
- izoxorik ravishda bosimi $2,02 \cdot 10^5 \text{ N/m}^2$ bosimgacha yetganda;

e) adiabatik ravishda $2,026 \cdot 10^5 \text{ N/m}^2$ siqilganda $Q, A, \Delta U, \Delta H$ qiymatlarini aniqlang. CO_2 ideal gazlar qonuniga bo'ysunadi deb faraz qiling. $C_p = 37,1 \text{ J/mol} \cdot \text{grad}$ ga teng.

Yechish. a) *izotermik kengayish:*

$\Delta U = C_v dT$ va $\Delta H = C_p dT$ bo'lganligidan izotermik jarayonda $\Delta U = 0$ va $\Delta N = 0$ ga teng bo'ladi.

(1.2) tenglamaga muvofiq, $dU = 0$ bo'lganligidan izotermik jarayonda $A = Q$ teng bo'ladi. (1.14) tenglamadan A, Q aniqlanadi:

$$Q = A = 2,3nRT \lg \frac{V_2}{V_1}, \text{ bu tenglamani yechish uchun, avvalo,}$$

n (mol soni) va V_1 (gazning oldingi hajmi) ni aniqlash kerak.

$$n = \frac{m}{M} = \frac{100}{44} = 2,27 \text{ mol, bunda } M - \text{CO}_2 \text{ ning molekular}$$

massasi. Boshlang'ich hajm (V_1) $V_1 p_1 = nRT$ tenglamadan foydalanib aniqlanadi:

$$V_1 = \frac{nRT}{p_1} = \frac{2,27 \cdot 8,314 \cdot 273}{1,013 \cdot 10^5} = 0,0509 \text{ m}^3$$

va nihoyat:

$$Q = A = 2,3 \cdot 2,27 \cdot 8,314 \cdot 273 \lg \frac{0,2}{0,0509} = 7070 \text{ J} = 7,07 \text{ kJ};$$

b) *izobarik jarayon* (1.16) tenglamasidan:

$$Q_p = \Delta H = nC_p(T_2 - T_1) = \frac{nC_p T_1}{V_1} (V_2 - V_1)$$

$$\frac{V_2}{V_1} \cdot \frac{V_2}{T_2} = \frac{V_1}{T_1} \text{ dan } T_2 = T_1 \frac{V_2}{V_1} \text{ ligi hisobga olinganda,}$$

$$Q_p = \Delta H = \frac{nC_p T_1}{V_1} (V_2 - V_1) = \frac{2,27 \cdot 37,2 \cdot 273}{0,059} (0,2 - 0,059) = 67400 \text{ J} = 67,4 \text{ kJ}.$$

Gaz izobar kengaygandagi bajarilgan ish (1.16) tenglamaga muvofiq:

$$A = p(V_2 - V_1) = 1,013 \cdot 10^5 (0,2 - 0,0509) = 1500 \text{ J} = 15,0 \text{ kJ};$$

d) *izoxorik jarayon*. Jarayonda hajm o'zgarmaganligidan (I.3) tenglamaga muvofiq $A = 0$ bo'ladi va bunda (I.12) va (I.15) tenglamalarga muvofiq:

$$Q_v = \Delta U = n C_v(T_2 - T_1) = \frac{n C_v T_1}{p_1} (p_2 - p_1)$$

$$C_p = C_v + R \text{ bo'lganligidan } C_v = C_p - R = 37,1 - 8,314 = 28,8 \text{ J/mol} \cdot \text{grad}.$$

$$Q_v = \Delta U = \frac{2,27 \cdot 22,8 \cdot 273}{1,013 \cdot 10^5} (2,026 \cdot 10^5 - 1,012 \cdot 10^5) = 17900 \text{ J} = 17,9 \text{ kJ}.$$

ΔH ni (I.16) tenglamadan izoxorik jarayon uchun foydalanib:

$$\Delta H = \Delta U + V(p_2 - p_1) = 17,9 + 0,0509 (2,026 - 1,13) \cdot 10^5 = 2,3 \text{ kJ}$$

ni hosil qilamiz;

e) *adiabatik jarayon*. Bu jarayonda $Q = 0$ bo'lganligidan (I.2) va (I.17) tenglamalarga muvofiq:

$$A = \Delta U = n C_v (T_1 - T_2) = \frac{n R T}{\gamma - 1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} \right] \text{ bo'ladi.}$$

γ — koeffitsiyent:

$$\gamma = \frac{C_p}{C_v} = \frac{37,1}{28,8} = 1,29$$

va

$$A = \Delta U = \frac{2,27 \cdot 8,314 \cdot 273}{1,29 - 1} \left[1 - \left(\frac{2,03}{1,01} \right)^{\frac{1,29 - 1}{1,29}} \right] = 2970 \text{ J} = 2,97 \text{ kJ}.$$

(I.11) tenglamadan:

$$\Delta H = \Delta U + (Vp) = U + (V_2 p_2 - V_1 p_1),$$

oxirgi hajm V_2 (I.11) tenglamadan ($p_1 V_1^\gamma = p_2 V_2^\gamma$) aniqlanadi.

$$\begin{aligned} \Delta H &= \Delta U + p_1 V_1 \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} = \\ &= 2,97 + 1,013 \cdot 10^5 \cdot 0,0509 \left[\left(\frac{2,03}{1,01} \right)^{\frac{\gamma-1}{\gamma}} \right] 10^5 = 3,83 \text{ kJ}. \end{aligned}$$

4. 6 g toluol bug‘latilganda Q , A , ΔU , ΔH larning qiymatlarini aniqlang. Toluolning qaynash harorati 383 K, bug‘lanish issiqligi 33,6 kJ/mol. Bug‘ni ideal gaz deb faraz qiling. Suyuqlik hajmi bug‘ hajmiga nisbatan juda kichik bo‘lganligidan, uni hisobga olmasa ham bo‘ladi.

Yechish. Bug‘lanish jarayoni izobarik ($p = \text{const}$) jarayon bo‘lganligidan (I.12) tenglamaga muvofiq:

$$Q_p = \Delta H n \cdot l = \frac{m}{M} \Delta H,$$

M — molekular massa = 92,14, l — bug‘lanish issiqligi.

$$Q = n \Delta H = \frac{6}{92,14} \cdot 33,6 \cdot 10^3 = 2,19 \cdot 10^3 \text{ J}.$$

Bajarilgan ish A izobarik jarayonda (I.16) tenglamaga muvofiq:

$$A = p(p_b - V_s) = p V_2 = n R T = \frac{6,8,134,383}{92,14} = 203 \text{ J},$$

bunda: V_b — bug‘ va suyuqlik hajmi.

ΔU ni (I.11) tenglamaga muvofiq:

$$\Delta H = \Delta(U + pV) = \Delta U + pV_b; \quad \delta A = p dV$$

va

$$\Delta U = \Delta N - pV_b = \Delta H - A = 2190 - 203 = 1987 \text{ J bo'ladi.}$$

5. 1 mol N_2 va 3 mol H_2 aralashmasi $T_1 = 298 \text{ K}$ dan $T_2 = 500 \text{ K}$ gacha qizdiriladi. Bunda ichki energiya va entalpiyaning qanchaga o'zgarishini aniqlang.

Moddalar issiqlik sig'implari haroratga bog'liq holda quyidagicha o'zgaradi:

$$C_{p,N_2} = 29,176 \cdot 10^3 - 0,8380 T + 2,0431 \cdot 10^{-3} T^2 \times \\ \times \text{J/mol} \cdot \text{grad.}$$

$$C_{p,H_2} = 27,3159 \cdot 10^3 - 5,2337 T - 0,004187 \cdot 10^{-3} T^2 \times \\ \times \text{J/mol} \cdot \text{grad.}$$

Yechish.

$$\Delta H = \Delta H_{N_2} + \Delta H_{H_2} = \int_{298}^{500} C_{p,N_2} dT + 3 \int_{298}^{500} C_{p,H_2} dT = \int_{298}^{500} (C_{p,N_2} + C_{p,H_2}) \cdot dT = \\ = \int_{298}^{500} \left[29,176 \cdot 10^3 - 0,8380T + 2,031 \cdot 10^{-3} T^2 \right] + 3 \left[27,3159 \cdot 10^3 - \right. \\ \left. - 5,2337T - 0,004187 \cdot 10^{-3} T^2 \right] - 0,004187 \cdot 10^{-3} T^2 \Big] \cdot dT = \\ = 23852,88 \cdot 10^3 \text{ J.}$$

ΔU aniqlanadi:

$$\Delta U = U_2 - U_1; \quad U_1 = H_1 - p_1 V_1; \quad U_2 = H_2 - p_2 V_2;$$

$$\Delta H = \Delta H_2 - \Delta H_1;$$

$$\Delta U = \Delta H - p_2 V_2 + p_1 V_1 = \Delta H - (n_{N_2} + n_{H_2}) RT_2 + (n_{N_2} + n_{H_2}) RT_1 = \\ = \Delta H - 4RT_2 + 4RT_1 = 23852,88 \cdot 10^3 - 4.8314 \cdot 10^3 (500 - 298) = \\ = 174134,36 \cdot 10^3 \text{ J.}$$

6. Gaz (turg'un bosimda) 10 litrdan 16 litrgacha kengaygan va bu jarayonda 300 kal (1256,1 J) issiqlik yutilgan. Ichki energiyaning o'zgarishini aniqlang.

Yechish. (I.2) tenglamaga muvofiq:

$$\begin{aligned}\Delta U &= Q - A; \quad Q = 300 \text{ kal} = 1256,1 \text{ J} \\ A &= p(V_2 - V_1) = 1 \cdot (16 - 10) = 6 \cdot 1 \text{ atm} = \\ &= 6 \cdot 1,0133 \cdot 10^2 = 607,98 \text{ J} \\ \Delta U &= Q - A = 1256,1 - 607,98 = 649,02 \text{ J}.\end{aligned}$$

7. Boshlang'ich bosimi $p = 760 \text{ mm sim. ust.}$ bo'lgan 1 m^3 havoni turg'un hajmda 0°C dan 1°C gacha isitish uchun qancha issiqlik kerak bo'ladi? Normal sharoitda havoning zichligi $d = 0,00129 \text{ g/km}^3$. Turg'un bosimdagi solishtirma issiqlik sig'imi $C_p = 0,24 \text{ g/grad}$ va $\frac{C_p}{C_v} = 1,4$.

$$Q = mC_v dT,$$

bunda: m — havo massasi.

$$\begin{aligned}d &= \frac{m}{V}; \quad m = dV = 1,29 \cdot 10^{-3} \cdot 10^6 = 1,29 \cdot 10^3 \text{ J} \\ C_p/C_v &= 1,4 \quad \text{dan} \quad C_v = \frac{0,24}{1,4} = 0,172.\end{aligned}$$

$$\text{Demak, } Q = 1,29 \cdot 10^3 \cdot 0,172 \cdot 1 = 222 \text{ kal}.$$

MASALALAR

1. 12 g geliy 250 K dan 400 K gacha qizdirilganda uning ichki energiyasi va entalpiyasi qanchaga o'zgaradi? $C_v = \frac{3}{2} R$ ga teng.

2. $1,013 \cdot 10^5 \text{ Pa}$ bosimda turgan va $67,2 \cdot 10^{-3} \text{ m}^3$ hajmni ishg'ol qilgan 6 g vodorod turg'un hajmda ichki energiyasi 8650 J ga

ortguncha qizdirilgan. $C_{p,H_2} = 28,83 \text{ J/mol}$ ga teng. Oxirgi bosim qanchaga teng?

3. 2 mol ideal gaz turg'un bosimda 5000 J ish bajarguncha qizdirilgan. Ichki energiyasi va entalpiyasi qanchaga o'zgaradi? $C_v = \frac{5}{2} R$ ga teng.

4. 0,12 kg vodorod va 1,4 kg azotdan iborat gaz aralashmasi $1,10 \cdot 13 \cdot 10^6 \text{ Pa}$ bosim ostida turibdi. Shu aralashmaning 250 K dagi bosimi $1,10 \cdot 13 \cdot 10^5 \text{ Pa}$ bosimgacha izotermik ravishda kengaytirilgan. Gazlarni ideal gazlar deb faraz qiling. Gazlar bajargan ish (A) qanchaga teng?

5. Kislorod va azotdan iborat 0,02 m³ havo turg'un bosim ($1,0130 \cdot 10^5 \text{ N/m}^2$) da 27° dan 227°C gacha isitilgan. Havo kengayganda bajargan ishi va yutilgan issiqlik qiymatini aniqlang. Kislorod va azotning chin molar issiqlik sig'imi:

$$C_p = 27,2 + 6,00 \cdot 10^{-5} T \text{ J/mol} \cdot \text{grad}.$$

6. CO₂ ning solishtirma izobarik issiqlik sig'imi 0,202 kal/g · grad. C_p/C_v nisbatni aniqlang.

7. Turg'un bosimda CO₂ ning o'rtacha issiqlik sig'imi $\bar{c}$:

$$\bar{c} = 0,2398 + 2,155 \cdot 10^{-5} T + 4,64 \cdot 10^{-8} T^2.$$

500°C da CO₂ ning molar chin issiqlik sig'imini aniqlang.

8. CaO ning molar chin issiqlik sig'imining haroratga bog'liqlik tenglamasi:

$$C_p = 11,67 + 1,08 \cdot 10^{-3} T - 1,56 \cdot 10^{-5} T^2.$$

10 kg CaO ni 0° dan 900° gacha qizdirish uchun ketgan issiqlik miqdorini aniqlang.

9. Turg'un bosimda 1 kg temir (III) oksid (Fe_2O_3) ni 0° dan $t^\circ\text{C}$ gacha qizdirish uchun ketgan issiqlik Q :

$Q = 184,2 + 0,054 \cdot t^2$. Molar issiqlik sig'imining haroratga bog'liqlik tenglamasini keltirib chiqaring.

10. 0°C va 5 atm bosimda turgan 2 l azot izotermik ravishda 1 atm gacha kengaytirilgan. Gaz bajaragan ishni (A) Joullda va yutilgan issiqlikni kaloriyada aniqlang.

11. 20 g etil spirti qaynash haroratida bug'latilganda uning ichki energiyasi o'zgarishini aniqlang. Spirtning solishtirma yashirin bug'lanish issiqligi 205 kal/g, qaynash haroratida bug'ning solishtirma hajmi $607 \text{ sm}^3/\text{g}$. Suyuqlik hajmini hisobga olmag.

12. 15°C va $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda $0,625 \text{ m}^3$ hajmdagi havo $0,1 \text{ m}^3$ gacha kengaytirilgan. Bajarilgan ish va oxirgi bosimni aniqlang.

13. 268°C va $9,32 \cdot 10^4 \text{ N/m}^2$ bosimdagi gaz hajmini, $0,5 \text{ m}^3$ da 4 m^3 gacha kengaytirilganda bajarilgan ish va issiqlikni aniqlang.

14. 2 g ClO_2 298 K dan 800 K gacha qizdirilganda entalpiyaning o'zgarishini aniqlang.

Bunda issiqlik sig'imi harorat bilan quyidagicha o'zgaradi:

$$C_p = 46,94 + 34,32 \cdot 10^{-3} T - 11,3 \cdot 10^{-5} T^{-2}.$$

15. $3 \cdot 10^3$ mol ammiak turg'un bosimda 273 K dan 473 K gacha isitilgan. Buning uchun kerak bo'lgan issiqlikni aniqlang. Issiqlik sig'imi harorat bilan quyidagicha o'zgaradi:

$$C_p = 29,8 + 25,48 \cdot 10^{-3} T - 1,67 \cdot 10^{-4} T^{-2}.$$

16. 1 kg CO_2 turg'un bosimda 200°C gacha qizdirilganda qancha ish bajaradi?

17. 450 g suv bug'i 100°C da suvga aylantirilgan. Suvning yashirin bug'lanish issiqligi 530 kal/g ga teng. Bu jarayonda A , Q va ΔU ni aniqlang.

18. Normal sharoitda ($T = 298$; $p = 1 \text{ atm}$) da 5 l ideal gaz turg'un hajmda 600°C gacha qizdirilgan. Bunga qancha issiqlik ketdi va oxirgi bosim qanchaga teng?

19. 1 kmol CO_2 ni izotermik ravishda 20°C da $1,02 \cdot 10^5$ dan $35,70 \cdot 10^5 \text{ N/m}^2$ bosimgacha siqish uchun qancha ish bajariladi?

20. 1 g CO_2 va 1 g H_2 dan iborat aralashma turg'un bosimda 275 K dan 400 K gacha qizdirilgan. CO_2 va H_2 ning molar issiqlik sig'imi (C_p) mos ravishda $\frac{5}{2}R$ va $\frac{7}{2}R$ ga teng. A , ΔH , ΔU , Q ning qiymatini aniqlang.

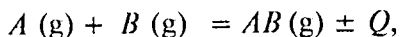
21. Normal bosimda butanning yashirin bug'lanish issiqligi 224 kJ/mol , butanning qaynash harorati $272,6 \text{ K}$ ga teng. $9,8 \text{ g}$ butan bug'langandagi Q , A , ΔU va ΔH ning qiymati qanchaga teng bo'ladi? Bug' hajmiga nisbatan suyuq butanning hajmi inobatga olinmasa ham bo'ladi. Bug'ni ideal gaz deb faraz qiling.

22. 17°C da 10 g kislorod adiabatik ravishda $0,008$ dan $0,005 \text{ m}^3$ hajmgacha siqilgan. Oxirgi harorat, sarflangan ish, ichki energiya va entalpiyaning o'zgarishini aniqlang.

II bob

TERMOKIMYO

Termokimyo termodinamika I bosh qonunining kimyoviy reaksiyalarga tatbiqini o'rganadi. Hamma kimyoviy reaksiyalarda issiqlik ajraladi (yoki yutiladi), ya'ni kimyoviy energiya issiqlik energiyasiga aylanadi. Har qanday jarayonda, shu jumladan, kimyoviy reaksiyalarda chiqqan (yoki yutilgan) issiqlik **issiqlik effekti** deyiladi. Sistemadan ajralgan issiqlik minus (—), yutilgan issiqlik (+) ishora bilan ifodalanadi. Termokimyoviy reaksiyalarda moddaning agregat holati: gaz (g), suyuqlik (s), qattiq (q) va issiqlik effekti ko'rsatib yoziladi:



bunda (+) ishorasi endotermik, (—) ishorasi ekzotermik reaksiyalar uchun xosdir.

(I.2) tenglamaga muvofiq reaksiya (turg'un hajmda) izoxorik ravishda olib borilganda:

$$Q_v = \Delta U, \quad (II.1)$$

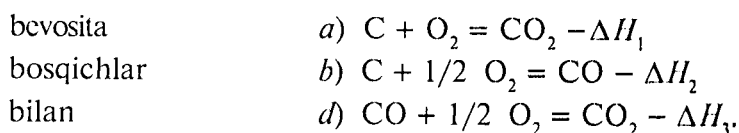
izobarik (turg'un bosimda) olib borilganda:

$$Q_p = \Delta H, \quad (II.2)$$

Q_v , Q_p — izoxorik va izobarik issiqlik effekti deyiladi.

Jarayonning yo'nalishi (izoxorik yoki izobarik) ma'lum bo'lganligidan, sistemaning ma'lum holatga qanday yo'llar bilan kelganligiga bog'liq emas. Shunga ko'ra, ular holat funksiyalari — to'liq funksiyalar bo'ladi.

Gess qonuni. *Kimyoviy reaksiyalarning izoxorik yoki izobarik issiqlik effekti sistemaning boshlang'ich va oxirgi holatlariga bog'liq bo'lib, jarayonning o'tish yo'liga, qanday oraliq bosqichlar orqali borganligiga bog'liq emas.* CO_2 gazi C va O_2 dan ikki yo'l bilan: bevosita va CO — oraliq modda hosil bo'lishi orqali hosil qilinishi mumkin:



b va *d* tenglamalar qo'shilsa, *a* tenglama kelib chiqadi. Demak, $\Delta H_1 = \Delta H_2 + \Delta H_3$ bo'ladi. Bulardan ikkitasi ma'lum bo'lsa, uchinchisini hisoblab aniqlash mumkin.

Standart issiqlik effektlari. Turli termokimyoviy hisoblar taqqoslanganda issiqlik effektlari bir xil sharoitga keltirilgan bo'lishi kerak. 298 K (25°C) va $1,013 \cdot 10^5$ Pa (1 atm) shunday sharoit sifatida qabul qilingan. Bu sharoitdagi issiqlik effektlari *standart issiqlik effektlari* deyiladi. ΔU_{298}^0 va ΔH_{298}^0 belgisi bilan beriladi va 1 mol toza moddaga nisbatan hisoblangan bo'ladi. Bu qiymatlar ko'p modda (reaksiya)lar uchun ma'lumotnomalarda berilgan.

Issiqlik effekti ifodalari. Molekulaning hosil bo'lish issiqligi $\Delta H_{\text{h.b.i.}}$ (hosil bo'lish issiqligi), yonish issiqligi ΔH_{yon} va reaksiya issiqligi ΔH_r .

Hosil bo'lish issiqligi — 1 mol moddaning oddiy moddalardan hosil bo'lgandagi issiqlik effekti. Yonish issiqligi ΔH_{yon} — 1 mol modda yonganda ajralgan issiqlikdir.

Gess qonunidan ikkita xulosa kelib chiqadi:

$$\Delta H_p = (\sum n \Delta H_{\text{h.b.i.}})_{\text{mahs}} - (\sum n \Delta H_{\text{h.b.i.}})_{\text{dast}}, \quad (\text{II.3})$$

ya'ni reaksiya issiqlik effekti, mahsulotlarning hosil bo'lish issiqlik effektlari yig'indisidan dastlabki moddalarning hosil bo'lish issiqlik effektlari yig'indisining farqiga teng. Xuddi shunday:

$$\Delta H_p = (\sum n \Delta H_{\text{yon}})_{\text{dast}} - (\sum n \Delta H_{\text{yon}})_{\text{mahs}}. \quad (11.4)$$

Turli moddalarning standart hosil bo'lish va yonish issiqlik effektlari ma'lumotnomalarda berilgan.

Kirxgof qonuni. Issiqlik effektlari reaksiya olib borilgan haroratga bog'liq. Bu bog'lanish Kirxgof qonunida ifodalangan:

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \cdot dT, \quad (11.5)$$

$\Delta H_1, \Delta H_2$ — T_1 va T_2 haroratdagi issiqlik effektlari.

Odatda, ΔH_1 sifatida standart issiqlik effektlari olinadi. Bunda Kirxgof tenglamasi quyidagicha bo'ladi:

$$\Delta H_T = \Delta H_{298}^0 + \int_{298}^T \Delta C_p \cdot dT. \quad (11.6)$$

Bunda ΔH_T T haroratdagi issiqlik effekti, u holda

$$\Delta C_p = (\sum n C_p)_{\text{m}} - (\sum n C_p)_{\text{d}}. \quad (11.7)$$

Masalan, $A + B = C + D$ reaksiya borayotgan bo'lsa va moddalarning issiqlik sig'imining haroratga bog'liqligi (C_p quyidagi qiymatlarga ega bo'lsa:

a) $C_{p,A} = a_1 + b_1 T + c_1 T^2;$

b) $C_{p,B} = a_2 + b_2 T + c_2 T^2;$

d) $C_{p,C} = a_4 + b_4 T + c_4 T^2;$

e) $C_{p,D} = a_3 + b_3 T + c_3 T^2.$

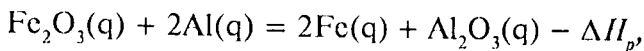
$\Delta C_p = (C_{p,C} + C_{p,D}) - (C_{p,A} + C_{p,B})$ teng bo'ladi, demak:

$$\Delta C_p = [(a_3 + b_3 T + c_3 T^2) + (a_4 + b_4 T + c_4 T^2)] - [(a_1 + b_1 T + c_1 T^2) + (a_2 + b_2 T + c_2 T^2)] = \Delta a + \Delta b T + \Delta c T^2.$$

$$\Delta H_O = \Delta H_{298}^0 + \int_{298}^T (\Delta a + \Delta b T + \Delta c T^2) dT = \Delta H_{298}^0 + \Delta a(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) + \frac{\Delta c}{3}(T^3 - 298^3).$$

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Quyidagi reaksiyaning issiqlik effekti (ΔH) ni aniqlang.



Al_2O_3 ning hosil bo'lish issiqlik effekti — 1670 kJ/mol,

Fe_2O_3 ning hosil bo'lish issiqlik effekti — 821 kJ/mol ga teng.

Yechish. (II.3) tenglamaga muvofiq reaksiyaning issiqlik effekti:

$$\Delta H_p = \Delta H_{\text{h.b.i.Fe}} = 0; \Delta H_{\text{h.b.i.Al}} = 0 \text{ ga teng.}$$

$$\Delta H_p = \Delta H_{\text{h.b.i.,Al}_2\text{O}_3} - \Delta H_{\text{h.b.i.,Fe}_2\text{O}_3} = (1 - 1670) - (-821) = -849 \text{ kJ/mol.}$$

2. Yuqorida berilgan reaksiyaning 650°C dagi issiqlik effektini issiqlik sig'imi ma'lumotlaridan foydalanib aniqlang. Reaksiyaning standart issiqlik effekti $(-1698) \cdot 10^6 \text{ J/mol}$.

$$C_{p,\text{Al}} = 0,745 + 44,89 \cdot 10^{-5} \text{ J/mol.}$$

$$C_{p,\text{Al}_2\text{O}_3} = 1,082 + 17,410 \cdot 10^{-5} T - 30,4 \cdot 10^3 T^{-2} \text{ J/g} \cdot \text{grad.}$$

$$C_{p,\text{Fe}} = 0,31 + 48 \cdot 10^{-5} T \text{ J/g} \cdot \text{grad.}$$

$$C_{p,\text{Fe}_2\text{O}_3} = 0,647 + 42,1 \cdot 10^{-5} T - 11,1 \cdot 10^3 T^{-2} \text{ J/g} \cdot \text{grad.}$$

Yechish. (II.6) va (II.7) tenglamalardan foydalanib, dastlab issiqlik sig'irlarini (J/kmol · grad.) keltirish kerak. Buning uchun qatorni o'ziga tegishli moddaning molekular massasiga ko'paytirish kerak:

$$M_{Al} = 26,98; \quad M_{Al_2O_3} = 91,92; \quad M_{Fe} = 55,84;$$

$$M_{Fe_2O_3} = 159,68;$$

$$C_{p,Al} = 20,2 \cdot 10^3 + 1213 \cdot 10^{-2} T, \text{ J/kmol} \cdot \text{grad.}$$

$$C_{p,Al_2O_3} = 110 \cdot 10^3 + 1775 \cdot 10^{-2} T - 3100 \cdot 10^6 T^2,$$

J/kmol · grad.

$$C_{p,Fe} = 17,9810^3 + 2680 \cdot 10^{-2} T, \text{ J/kmol} \cdot \text{grad.}$$

$$C_{p,Fe_2O_3} = 103,5 \cdot 10^3 + 6730 \cdot 10^{-2} T - 1773 \cdot 10^6 T^2,$$

J/kmol · grad.

$$T = 650 + 273 = 923.$$

$$\Delta H = \Delta H_{298}^0 + \Delta a(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) - \Delta C^1 \left(\frac{1}{T} - \frac{1}{298} \right).$$

Δa , Δb , Δc koeffitsiyentlar aniqlanadi.

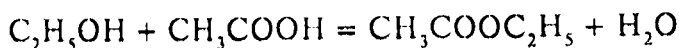
$$\Delta a = 0,8 \cdot 10^3; \quad \Delta b = 2021 \cdot 10^{-2}; \quad \Delta c' = 1325 \cdot 10^6 - 1$$

$$\text{va } \Delta H_{298} = -1698 \text{ J/kmol.}$$

$$\Delta H_{298} = -1698 \cdot 10^6 + 0,8 \cdot 10^3 \cdot 625 + 1010 \cdot 10^{-2} \cdot 7,64 \cdot 10^3 -$$

$$-1325 \cdot 10^6 \cdot 2,38 \cdot 10^{-3} = -1690 \cdot 10^5 \text{ J/kmol.}$$

3. Quyidagi reaksiyaning



standart issiqlik effektini aniqlang.

C_2H_5OH va CH_3COOH va $CH_3COOC_2H_5$ ning standart yonish issiqlik effektlari mos ravishda -1370 , -876 ; -2250 kJ/mol ga teng.

$$\Delta H_{yon, H_2O} = 0 \text{ ga teng.}$$

Y e c h i s h . (II.4) tenglamadan foydalanamiz:

$$\Delta H_p = (\sum n \Delta N_{yon})_d - (\sum n \Delta N_{yon})_m$$

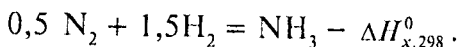
$$\begin{aligned} \Delta H_p &= (\Delta H_{yon, C_2H_5OH} + \Delta H_{yon, CH_3COOH}) - (\Delta H_{yon(CH_3COOC_2H_5)}) = \\ &= (-1370 - 876) - (-2250) = 4 \text{ kJ/mol.} \end{aligned}$$

4. Quyidagi tenglamalardan foydalanib:

$$a) 2H_2 + O_2 = 2H_2O - \Delta H_1; \quad \Delta H_1 = -571,65 \text{ kJ;}$$

$$b) 4NH_3 + 3O_2 = 6H_2O + 2N_2 - \Delta H_2; \quad \Delta H_2 = -1530,28 \text{ kJ.}$$

normal sharoitda ammiakning oddiy moddalardan standart hosil bo'lish issiqlik effektini aniqlang:



Y e c h i s h . Ammiak hosil bo'lish reaksiyasida H_2O va O_2 yo'q. Shuning uchun (a) va (b) tenglamalardan ularni chiqarib tashlash kerak, buning uchun (a) tenglamani 3 ga ko'paytirib, undan (b) tenglamani olib tashlaymiz:

$$6H_2 + 3O_2 - 4NH_3 - 3O_2 = 6H_2O + 3\Delta H_1 - 6H_2O - 2N_2 - \Delta H_2$$

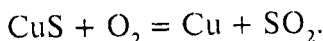
va 4 ga bo'lgandan so'ng:

$$0,5 N_2 + 1,5 H_2 = NH_3 + (3\Delta H_1 - \Delta H_2).$$

Demak:

$$\Delta H_{x,298} = (3\Delta H_1 - \Delta H_2)/4 = [3(-571,68)(-1570,98)/4 = -46,19 \text{ kJ/mol.}$$

5. Quyidagi reaksiyaning issiqlik effektini 727°C (1000 K) va $p = 1 \text{ atm}$ bosimda aniqlang:



CuS va SO₂ ning 25°C va 1 atm bosimda hosil bo'lish issiqlik effekti mos ravishda 11600 va 70960 kal/mol ga teng. Reaksiyada ishtirok etayotgan moddalarning izobarik molar issiqlik sig'imi:

$$C_{p(\text{CuS})} = 10,6 + 2,64 \cdot 10^{-3}T;$$

$$C_{p(\text{O}_2)} = 6,502 + 1,738 \cdot 10^{-3}T;$$

$$C_{p(\text{Cu})} = 5,43 + 11,4 \cdot 10^{-3}T;$$

$$C_{p(\text{SO}_2)} = 11,40 + 1,714 \cdot 10^{-3}T.$$

Yechish. 25°C (298 K) da CuS va SO₂ larning hosil bo'lish issiqlik effektlaridan reaksiyaning issiqlik effekti aniqlanadi.
(11.6) tenglamaga muvofiq:

$$\Delta H_{1000} = \Delta H_{298}^0 + \int_{298}^{1000} \Delta C_p \cdot dT.$$

Demak, oldin ΔH_{298}^0 va ΔC_p ni aniqlash kerak. (11.3) tenglamaga muvofiq:

$$\Delta H_{298}^0 = 70960 - 11600 = 59360 \text{ kal/mol.}$$

O₂ va Cu ning hosil bo'lish issiqlik effektlari $\Delta H_{x\text{O}_2} = \Delta H_{x\text{Cu}} = 0$.

Demak, ΔC_p quyidagicha aniqlanadi:

$$\Delta C_p = (C_{p,\text{Cu}} + C_{p,\text{SO}_2}) - (C_{p,\text{CuS}} + C_{p,\text{O}_2}) = 5,43 + 11,40 - 10,6 - 6,502 + \\ + [(11,41 + 1,714) - (2,61 - 1,738)] \cdot 10^{-3} T = -0,272 - 1,254 \cdot 10^{-3} T.$$

Endi yuqoridagi integral tenglama yechiladi:

$$\Delta H_{1000} = 59360 - \int_{298}^{1000} (-0,272 - 1,254 \cdot 10^{-3}) dT = 59360 + 0,272(1000 - \\ - 298) + \frac{1,254 \cdot 10^{-3}}{2} (1000^2 - 298^2) = -60122 \text{ kkal}.$$

6. Quyidagi ma'lumotlardan foydalanib, 80°C da benzolning molar yashirin bug'lanish issiqligini aniqlang. 0°C da benzolning yashirin bug'lanish issiqligi 7810 kal/mol, 0—81°C chegarasida benzol bug'ining solishtirma o'rtacha issiqlik sig'imi 0,299 kal/g, shu harorat chegarasida suyuq benzolning o'rtacha solishtirma issiqlik sig'imi 0,411 kal/grad.

Y e c h i s h . (II.6) tenglamaga muvofiq:

$$\Delta H_{80} = \Delta H_0 + \int_0^{280} \Delta C_p dT.$$

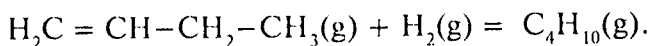
C_p solishtirma issiqlik sig'imini molar issiqlikka o'tkazish uchun solishtirma issiqlik sig'imini benzolning molekular massasi ($M = 80$) ga ko'paytirish kerak:

$$\Delta C_p = (0,299 - 0,411)80 = -8,736 \text{ kal/mol} \cdot \text{grad}.$$

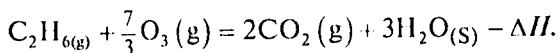
$$\Delta H_{80} = 7810 + \int_0^{80} -8,756 dT = 7810 - 8,756 \cdot 80 = 7111 \text{ kal/mol}.$$

MASALALAR

1. Buten-1 C_4H_8 va butan C_4H_{10} ning standart yonish issiqliklari mos ravishda -2719 kJ/mol va $-2879,2$ kJ/mol ga teng. Butenning vodorodlanish reaksiyasi standart issiqlik effektini aniqlang. H_2O ning standart hosil bo'lish issiqligi $-286,04$ kJ/mol.

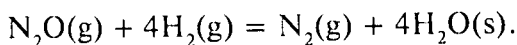


2. Etanning kislorodda standart yonish issiqligi $-156,10$ kJ/mol, ozonning standart hosil bo'lish issiqligi $142,3$ kJ/mol. Shu ma'lumotlardan foydalanib, etanning ozonda standart yonish issiqligini aniqlang:



3. Oktan $CH_3 - (CH)_6 - CH_3$ —standart yonish issiqligi $-5512,2$ kJ/mol, buten — 1 $CH_2 = CH - CH_2 - CH_3$ va butan $CH_3(CH_2)_2CH_3$ ning standart yonish issiqligi mos ravishda $-2719,0$ va $-2879,2$ J/mol ga teng. Shu ma'lumotlardan foydalanib, oktanning kreking (ajralish) reaksiyasi standart issiqlik effektini aniqlang.

4. Azot oksidi N_2O va suvning standart hosil bo'lish issiqlik effekti mos ravishda $9,667$ kJ/mol va $286,04$ kJ/mol ga teng. Standart sharoitda quyidagi reaksiyaning issiqlik effektini hisoblang:



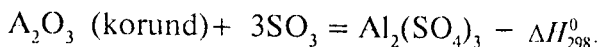
5. Rombik oltingugurtning monoklin oltingugurtga aylanishi, $S_{\text{romb}} \rightarrow S_{\text{monokl.}}$ reaksiyaning standart issiqlik effekti $0,297$ kJ/mol

ga teng. Quyidagi ma'lumotlardan foydalanib, bu jarayonning 450 K dagi o'tish issiqlik effektini aniqlang.

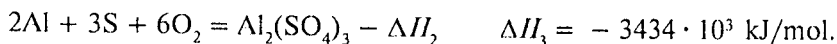
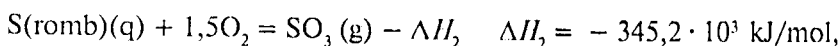
$$C_{p1 \text{ (rombik S)}} = 469 + 0,817 \cdot T \text{ J/kg} \cdot \text{grad},$$

$$C_{p2 \text{ (monoklin S)}} = 465 + 0,910 \cdot T \text{ J/kg} \cdot \text{grad}.$$

6. Quyidagi reaksiyaning standart issiqlik effektini aniqlang.



Dastlabki moddalar va mahsulotlarning standart hosil bo'lish issiqlik effekti quyidagicha:

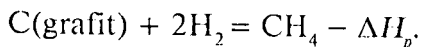


7. Quyidagi ma'lumotlardan foydalanib, metan (CH_4) ning hosil bo'lish standart issiqligini aniqlang. Metanning yonish issiqligi:

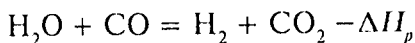
$$\Delta H_{\text{yon,CH}_4} = -890,964 \cdot 10^6 \text{ J/kmol},$$

$$\text{vodorodniki } \Delta H_{\text{yon,H}_2} = -286,043 \cdot 10^6 \text{ J/kmol};$$

uglerod grafitiniki $\Delta H_{\text{yon,C}} = -353,796 \cdot 10^6 \text{ kJ/mol}$. CH_4 ning hosil bo'lish reaksiyasi:

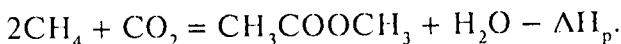


8. Vodorodning yonish issiqligi ($\text{H}_2 + 0,5\text{O}_2 = \text{H}_2\text{O}$) $\Delta H_{\text{H}_2} = -211,84 \text{ kJ/mol}$, CO yonish issiqligi ($\text{CO} + 0,5\text{O}_2 = \text{CO}_2$) $\Delta H_{\text{CO}} = -285,16 \text{ kJ/mol}$. Quyidagi reaksiyaning



issiqlik effektini aniqlang.

9. 500 K da gaz holidagi asetonning metan va CO_2 dan hosil bo'lish reaksiyasi issiqlik effektini aniqlang:

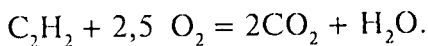


Quyidagi ma'lumotlar berilgan:

Modda	$\Delta H_{298}^0 \cdot 10^6$ J/kmol	$a \times 10^{-3}$	b	$C'_x \times 10^{-3}$	$C''_x \times 10^{-3}$
		J/kmol			
$\text{H}_2\text{O} (\text{g})$	-242,000	30,146	11,305	—	—
$\text{CH}_3\text{COOCH}_3 (\text{g})$	-216,796	22,489	201,926	—	63,576
CO_2	-398,706	44,173	9,044	-8,541	—
CH_4	-74,901	17,484	60,502	—	-1,118

(a , b , c' , c lar $C_p = f(T)$ bog'lanishni aniqlashda qo'llaniladigan koeffitsiyentlar).

10. C_2H_2 , CO_2 va $\text{H}_2\text{O}(\text{s})$ ning hosil bo'lish issiqlik effekti mos ravishda 54190, 94052 va 68317 kkal/molga teng. 5 mol C_2H_2 yonganda qancha issiqlik ajraladi?

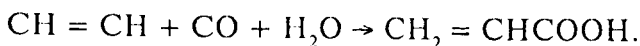


11. $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ — reaksiyaning issiqlik effekti 42498 kal. CaO va CO_2 ning hosil bo'lish issiqligi mos ravishda 151900 va 94052 kkal/mol. CaCO_3 ning hosil bo'lish issiqligini aniqlang.

12. Suv va suv bug'ining hosil bo'lish issiqligi mos ravishda $-285,8$ va $-241,8$ kJ/mol. 25°C da 1 mol suvning bug'lanish issiqligini aniqlang.

13. Amorf uglerod, grafit va olmosning yonish issiqliklari mos ravishda $-409,2$; $-394,6$ va $395,3$ kJ/g-atom: 1 — amorf uglerodning grafitga, 2 — amorf uglerodning olmosga; 3 — grafitning olmosga o'tish (allotropik aylanish) issiqligini aniqlang.

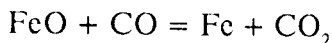
14. Akril kislota (suyuq holda hosil bo'luvchi) sintezi reaksiyasi:



Standart (1 atm va 298 K) sharoit uchun reaksiya effektini aniqlang. Reaksiyada ishtirok etgan moddalarning hosil bo'lish issiqliklari quyidagicha:

Modda	$\text{CH}=\text{CH}$	CO	H_2O	CH_2CHCOOH
ΔH_{298}^0 , kJ/mol	226,75	-110,50	-288,84	384,37

15. 1200 K va turg'un bosimda 100 kg temir (II) oksid (FeO), uglerod (II) oksid (CO) bilan qaytarilganda:



ajralgan issiqlik miqdorini aniqlang. Reagentlarning izobarik molar issiqlik sig'imi (C_p) quyidagi ifodaga teng:

$$C_{p,\text{Fe}} = 19,25 + 21,0 \cdot 10^{-3} T \text{ J/mol} \cdot \text{grad},$$

$$C_{p,\text{CO}_2} = 44,14 + 9,04 \cdot 10^{-3} T - 8,53 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad},$$

$$C_{p,\text{CO}} = 28,48 + 4,10 \cdot 10^{-3} T - 0,46 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad},$$

$$C_{p,\text{FeO}} = 52,80 + 6,21 \cdot 10^{-3} T - 3,19 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad}.$$

16. 1200°C da suvning molar bug'lanish issiqligini aniqlang. 100°C da suvning solishtirma bug'lanish issiqligi 539 kal/g · grad ga teng. Suv va suv bug'ining solishtirma issiqlik sig'imi mos ravishda 1,0 va 0,45 kal/g · grad ga teng.

17. 25°C va turg'un bosimda 1 g vodorodning yonib suv hosil qilishida 34158 kal issiqlik ajraladi. 25°C da suvning solishtirma yashirin bug'lanish issiqligi 584 kal/g · grad ga teng. Suv bug'i, vodorod va kislorodning molar issiqlik sig'imi quyidagi qiymatga ega:

$$C_{p,\text{H}_2\text{O}} = 7,2 + 2,7 \cdot 10^{-3} T \text{ kal/mol} \cdot \text{grad},$$

$$C_{p,\text{H}_2} = 0,907 + 0,12 \cdot 10^{-3} T \text{ kal/mol} \cdot \text{grad},$$

$$C_{p,\text{O}_2} = 5,052 + 5,69 \cdot 10^{-3} T \text{ kal/mol} \cdot \text{grad}.$$

18. 227°C va turg'un bosimda rux oksidning hosil bo'lish $\text{Zn} + \frac{1}{2} \text{O}_2 = \text{ZnO}$ reaksiyasining issiqlik effektini aniqlang. 25°C va turg'un bosimda uning hosil bo'lish issiqlik effekti 83170 kal/mol ga teng. Reaksiyada ishtirok etgan moddalarning molar issiqlik sig'imi qiymati quyidagicha (kal/mol · gradus hisobida):

$$C_{p,\text{ZnO}} = 11,71 + 1,22 \cdot 10^{-3} T,$$

$$C_{p,\text{Zn}} = 5,25 + 2,70 \cdot 10^{-3} T,$$

$$C_{p,\text{O}_2} = 5,75 + 3,34 \cdot 10^{-3} T.$$

19. $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}_{(s)}$ reaksiyaning 300 K dagi reaksiya issiqlik effekti 90, 72 kJ ga teng. Moddalarning molar issiqlik sig'imi:

$$C_{p,\text{CO}} = 28,41 + 4,10 \cdot 10^{-3} T - 0,46 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad},$$

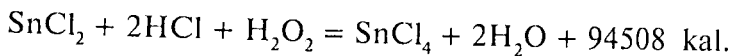
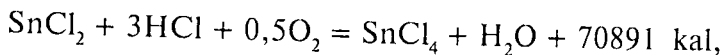
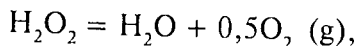
$$C_{p,\text{H}_2} = 27,28 + 3,26 \cdot 10^{-3} T + 0,502 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad},$$

$$C_{p,\text{CH}_3\text{OH}} = 27,28 + 3,26 \cdot 10^{-3} T + 0,502 \cdot 10^5 T^{-2} \text{ J/mol} \cdot \text{grad}.$$

500 va 1000 K da reaksiyaning issiqlik effektini aniqlang.

20. 15°C da etil spirtning suyuqlanish issiqligi 27,62 kJ/mol ga teng. 0°—75°C spirt va spirt bug'ining solishtirma o'rtacha issiqlik sig'imi mos ravishda 2,418 va 1,597 J/g · grad ga teng. 60°C da 500 g spirtning bug'lanishi uchun kerak bo'lgan issiqlik miqdorini aniqlang.

21. Quyidagi ma'lumotlardan foydalanib, vodorod peroksidning qaytarilish reaksiyasi issiqlik effektini aniqlang:



KO'P VARIANTLI MASALALAR

1. 298 K da a) $p = \text{const}$ va b) $V = \text{const}$ bo'lgan sharoitdagi reaksiya (A) ning issiqlik effektini aniqlang. (Moddalarning standart hosil bo'lish issiqlik effektini ma'lumotnomadan oling).

№	A reaksiya	№	A reaksiya
1	$2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}(\text{s})$	14	$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$
2	$4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O}(\text{s}) + 2\text{Cl}_2$	15	$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}(\text{s})$
3	$\text{NH}_4\text{Cl}(\text{q}) \pm \text{NH}_3 + \text{HCl}$	16	$2\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}(\text{s})$
4	$2\text{N}_2 + 6\text{H}_2\text{O}(\text{s}) = 4\text{NH}_3 + 3\text{O}_2$	17	$\text{CO} + \text{Cl}_2 = \text{COCl}_2(\text{g})$
5	$4\text{NO} + 6\text{H}_2\text{O}(\text{s}) = 4\text{NH}_3 + 5\text{O}_2$	18	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}(\text{s})$
6	$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	19	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}(\text{s})$
7	$\text{N}_2\text{O}_4 = 2\text{NO}_2$	20	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$
8	$\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}(\text{q})$	21	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$
9	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$	22	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$
10	$\text{Ca}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}_2$	23	$\text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}(\text{s})$
11	$\text{S}(\text{rom}) + 2\text{H}_2\text{O}(\text{s}) = \text{SO}_2 + 2\text{H}_2$	24	$\text{CH}_3\text{CHO}(\text{g}) + \text{H}_2 = \text{C}_2\text{H}_5\text{OH}(\text{s})$
12	$\text{S}(\text{rom}) + 2\text{CO}_2 = \text{SO}_2 + 2\text{CO}$	25	$\text{C}_6\text{H}_6(\text{s}) + 3\text{H}_2 = \text{C}_3\text{H}_{12}$
13	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$		

2. Quyidagi jadvalda keltirilgan moddalarning standart $T' = 298 \text{ K}$ va $1,0133 \cdot 10^5 \text{ Pa}$ da hosil bo'lish issiqlik effektini yonish issiqligidan (ΔH_{yon}) foydalanib aniqlang. Yonish mahsulotlari $\text{CO}_2(\text{gaz})$, $\text{H}_2\text{O}(\text{s})$ va $\text{N}_2(\text{g})$. Oddiy moddalarning yonish issiqlik effektlari:

$\text{C}(\text{graf}) + \text{O}_2 = \text{CO}_2(\text{g}) - 393,795 \cdot 10^3 \text{ J/mol}$, $\text{N}_2 + 0,5\text{O}_2 = \text{H}_2\text{O}(\text{s}) - 286,043 \cdot 10^3 \text{ J/mol}$.

№	Modda	$\Delta H_{\text{yon}} \cdot 10^{-3}, \text{ J/mol}$	№	Modda	$\Delta H_{\text{yon}} \cdot 10^{-3}, \text{ J/mol}$
1	$\text{CH}_4\text{N}_2\text{O}(\text{q})$ mochevina	-634,749	11	$\text{C}_4\text{H}_{10}(\text{g})$ butan	-23799,191
2	$\text{CH}_3\text{NO}_2(\text{s})$ nitrometan	-709,278	12	$\text{C}_5\text{H}_{12}\text{O}(\text{s})$ amil spirt	-3323,222
3	$\text{C}_2\text{H}_5\text{NO}_2(\text{s})$ glitkol	-931,852	13	$\text{C}_6\text{H}_6\text{O}(\text{q})$	-3024,851
4	$\text{C}_2\text{H}_6\text{O}_2(\text{s})$ etilenglikol	-1180,315	14	$\text{C}_6\text{H}_6\text{O}_2(\text{g})$ gidroksinon	-2662,519
5	$\text{C}_3\text{H}_8\text{O}_2(\text{s})$ glitserin	-1162,239	15	$\text{C}_6\text{H}_7\text{N}(\text{s})$ anilin	-3398,588

6	C_2H_7N (s) dimetiamin	-1774,229	16	$C_7H_6O_2$ (q) benzoyin kislota	-3229,014
7	C_3H_6O (s) aseton	-1787,012	17	C_5H_5 (s) piridin	-2577,140
8	C_4H_6 (g) butadien	-2595,647	18	$C_5H_{10}O_2$ (s) valerian kislota	-2853,769
9	C_3H_3N (g)	-1945,699	19	C_7H_8 (s) toluol	-3950,760
10	C_3H_8O (s)	-2011,853	20	C_8H_{18} (g) oktan	-5516,163

3. Quyidagi jadvalda keltirilgan haroratlardagi reaksiyalarning issiqlik effektini aniqlang ($T' = 298$ K dagi standart issiqlik effekti va issiqlik sig'imini ma'lumotnomadan oling).

№	Reaksiya	T, K
1	$2H_2 + CO = CH_3OH$ (g)	500
2	$4HCl + O_2 = 2H_2O$ (g) + $2Cl_2$	600
3	NH_4Cl (q) = NH_3 + HCl	500
4	$2N_2 + 6H_2O = 4NH_3 + 3O_2$	1200
5	$4NO + 6H_2O$ (g) = $4NH_3 + 5O_2$	800
6	$2NO_2 = 2NO + O_2$	500
7	$Mg(OH)_2 = MgO + H_2O$	400
8	$CaCO_3 = CaO + CO_2$	700
9	$N_2O_4 = 2NO$	400
10	$Ca(OH)_2 = CaO + H_2O$ (g)	350
11	$1/2S_2 + 2H_2O$ (g) = $SO_2 + 2H_2$	900
12	$1/2S_2 + 2CO_2 = SO_2 + 2CO$	800
13	$2SO_2 + O_2 = 2SO_3$	600
14	$SO_2 + Cl_2 = SO_2Cl_2$ (g)	400
15	$CO + 3H_2 = CH_4 + H_2O$ (g)	900
16	$4CO + 2SO_2 = S_2$ (g) + $4CO_2$	700

17	$\text{CO} + \text{Cl}_2 = \text{COCl}_2 (\text{g})$	400
18	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} (\text{g})$	600
19	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} (\text{g})$	800
20	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$	500

III bob

TERMODINAMIKANING IKKINCHI QONUNI

Birinchi (bosh) qonunda energiyaning bir xili boshqasiga aylanishi bilan boradigan jarayon sodir bo'lsa, energiyaning o'zgarishi ekvivalentlik qonuniga bo'ysungan holda bo'ladi. Lekin bu jarayon umuman yoki ma'lum sharoitda boradimi yoki yo'qmi, degan savolga javob bermaydi. Ikkinchi qonun bu kamchilikni to'ldiradi va uning asosiy vazifasi jarayon (reaksiya)ning yo'nalishi, ya'ni borish-bormasligini, qaysi tomonga borishini oldindan aytib berish va muvozanat qachon qaror topishi (muvozanatning termodinamik shartlari)ni aniqlashdan iboratdir.

Bu savollarga termodinamik funktsiya (potensial)lar deb atalgan to'rtta kattalikning — *entropiya* (S), *Gelmgols funktsiyasi* (F), *Gibbs funktsiyasi* (G) va *kimyoviy potentsiallarining* (μ) turli jarayonlarda o'zgarishini aniqlash (hisoblash) orqali javob olinadi.

Jarayonlar klassifikatsiyasi

O'z-o'zidan boradigan va o'z-o'zidan bormaydigan jarayonlar. Tabiatdagi real jarayonlar bir tomonga yo'nalgan bo'lib, o'z-o'zidan boradi, masalan, issiqlik issiq jismdan sovuq jismga o'tadi, turli bosimdagi gazlar o'z bosimini tenglashtiradi, elektr yuqori potentsialdan past potentsial tomon oqadi va hokazo. Bunday jarayonlarda sistema ish bajaradi. Bu jarayonlarning aksi *o'zicha bormaydigan jarayonlar* deyiladi. Masalan, issiqlikning sovuq jismdan issiq jismga o'tishi (sovitkichlarda). Lekin bunday jarayonlarning borishi uchun energiya sarflanishi kerak. Demak, ularni o'zicha boruvchi jarayonlar bilan birga olib borish kerak.

Termodinamik qaytar va noqaytar (qaytmas) jarayonlar. Qaytar jarayonda jarayondan so'ng sistema va sistemaning atrofi o'zining oldingi holatiga keladi. Jarayon qaytar bo'lishi uchun: a) jarayon bir yo'nalishda borib, xuddi shunday qaytishi; b) jarayonning hamma bosqichi muvozanat holatidan cheksiz kichik farq qilishi; d) jarayonning hamma bosqichi qaytar bo'lishi; e) qarama-qarshi kuchlarning farqi cheksiz kichik bo'lishi; f) jarayon tezligi cheksiz kichik bo'lishi kerak. Termodinamik qaytar jarayon ideal jarayondir (tabiatda bunday jarayon yo'q). Lekin unga ma'lum darajada yaqinlashish mumkin. Yuqoridagi shartlar bajarilmasa, jarayon qaytmas (noqaytar) bo'ladi. Tabiatdagi jarayonlar qaytmas jarayonlardir.

Issiqlik va ishning bir-biriga aylanishi. Ish issiqlikka to'liq aylanadi, lekin issiqlik ishga to'la o'tmaydi (faqat bir qismi o'tadi). Agar T_1 issiqlik manbayining harorati va T_2 — sovitkichning harorati, Q_1 — issiqlik manbayidan olingan va Q_2 — sovitkichga berilgan issiqlik bo'lsa, u holda bajarilgan ish (A) teng bo'ladi:

$$A = Q_1 - Q_2. \quad (\text{III. 1})$$

Bundan foydali ish koeffitsiyenti:

$$\eta = \frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1}. \quad (\text{III. 2})$$

Tenglik alomati qaytar va tengsizlik ishorasi qaytmas jarayon uchun xosdir.

Entropiya (S). Entropiya izolirlangan sistemada boradigan jarayonlar uchun qo'llaniladi. Entropiya holat funksiyasi bo'lib (to'liq funksiya), uning o'zgarishi faqat sistemaning dastlabki va oxirgi holatiga bog'liq, jarayonning tabiatiga bog'liq emas. Uning

o'zgarishi qaytar va qaytmas jarayonda bir xil bo'ladi va hisoblarda qaytar jarayon tenglamasidan foydalanish mumkin. Agar jarayon bir qancha bosqichdan iborat bo'lsa, jarayonda entropiyaning o'zgarishi hamma bosqichlar entropiyasining o'zgarishi yig'indisiga teng bo'ladi:

$$\Delta S = \Delta S_1 + \Delta S_2 + \dots, \quad \Delta S = \sum \Delta S_i. \quad (\text{III.3})$$

Sistema bir holatdan ikkinchi holatga o'tgandagi entropiya o'zgarishi

$$dS \geq \frac{\delta Q}{T}; \quad \Delta S = \int \frac{\delta Q}{T} \quad (\text{III.4})$$

va

$$TdS \geq \delta Q, \quad (\text{III.5})$$

tenglik «=» ishorasi qaytar va «>» ishorasi qaytmas jarayon uchun xos. (I.2), (III.4), (III.5) tenglamalardan

$$TdS \geq dU + \delta A \quad (\text{III.6})$$

va

$$TdS \geq dU + pdV \quad (\text{III.7})$$

ni hosil qilamiz.

Entropiya turli jarayonda quyidagicha o'zgaradi:

$$\Delta S \geq 0. \quad (\text{III.8})$$

«=» ishorasi qaytar va «>» ishorasi qaytmas jarayonga mansub. Demak, izolirlangan sistemada boradigan qaytar jarayonda entropiya o'zgarmaydi ($S_1 = S_2$) va qaytmas jarayonlar entropiyaning ortishi

tomon boradi ($S_2 > S_1$). Entropiya maksimal qiymatga ega bo'lganda muvozanat qaror topadi:

$$\Delta S = 0; \quad d_2 S < 0. \quad (\text{III.9})$$

Entropiyaning turli jarayonlarda o'zgarishi quyidagicha hisoblaniladi:

a) izotermik ($T = \text{const}$) jarayonlarda — fizikaviy o'zgarishlarda bir agregat holatdan boshqa agregat holatga o'tish va hokazo jarayonlarda n mol modda uchun entropiyaning o'zgarishi:

$$\Delta S = n \int_1^2 \frac{\delta Q}{T} = \frac{1}{T} n \int_1^2 \delta Q, \quad (\text{III.10})$$

Q , ΔH — o'tish issiqliklari; T — o'tish harorati;

b) izobarik ($p = \text{const}$) jarayonda n mol modda T_1 dan T_2 gacha isitilganda:

agar bitta modda bo'lsa:

$$\Delta S = S_2 - S_1 = n \int_{T_1}^{T_2} \frac{C_p dT}{T}, \quad (\text{III.11})$$

reaksiya uchun esa:

$$\Delta S = n \int_{T_1}^{T_2} \frac{\Delta C_p dT}{T};$$

$$\Delta C_p = \left(\sum n_{yon} C_{r,g} \right)_{\text{mahs}} - \left(\sum n_{yon} C_{p,i} \right)_{\text{dast}}.$$

ΔC_p — mahsulotlarning issiqlik sig'imi yig'indisidan dastlabki moddalar issiqlik sig'imi yig'indisi ayirmasiga teng.

Agar molar issiqlik sig'imi haroratga bog'liq emas, ya'ni turg'un deb faraz qilinsa:

$$\Delta S = nC_p \int_{T_1}^{T_2} \frac{dT}{T} = 2,3nC_p \lg \frac{T_2}{T_1}. \quad (\text{III.12})$$

Agar $C_p = \varphi(T)$, ya'ni haroratga bog'liq bo'lsa:

$$C_p = a + bT + cT^2 + \dots$$

Demak,

$$\begin{aligned} \Delta S &= n \int_{T_1}^{T_2} \frac{C_p dT}{T} = n \int_{T_1}^{T_2} \frac{1}{T} (a + bT + cT^2) dT = n \int_{T_1}^{T_2} \frac{a dT}{T} + \\ &+ (bdT + cTdT) = 2,3na \lg \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2); \end{aligned} \quad (\text{III.13})$$

d) n — mol ideal gaz $p = \text{const}$ da T_1 dan T_2 gacha isitilganda hajmi V_1 dan V_2 gacha kengaysa, entropiyaning o'zgarishi quyidagicha hisoblanadi:

$$\Delta S = 2,3nC_v \lg \frac{T_2}{T_1} + 2,3nR \lg \frac{V_2}{V_1} \quad (\text{III.14})$$

yoki C_v harorat o'zgarishi bilan o'zgarsa, ya'ni $C_v = a + bT + cT^2$ teng bo'lsa, entropiyaning o'zgarishi quyidagicha aniqlanadi:

$$\Delta S = 2,3na \lg \frac{T_2}{T_1} + nb(T_2 - T_1) - \frac{nc}{2}(T_2^2 - T_1^2) + 2,3nR \lg \frac{V_2}{V_1}. \quad (\text{III.15})$$

Agar n — mol gaz izotermik ($T = \text{const}$) ravishda V_1 dan V_2 gacha kengaysa:

$$\Delta S = 2,3R \lg \frac{V_2}{V_1}. \quad (\text{III.16})$$

Agar $V = \text{const}$ da $T_1 \rightarrow T_2$ va $p_1 \rightarrow p_2$ ga o'zgarsa:

$$\Delta S = 2,3nC_p \lg \frac{T_2}{T_1} = 2,3nR \lg \frac{p_2}{p_1}. \quad (\text{III.17})$$

Agar n mol ($T = \text{const}$) da ideal gaz p_1 dan p_2 gacha siqilsa:

$$\Delta S = 2,3nR \lg \frac{p_1}{p_2} \quad (\text{III.18})$$

yoki

$$\Delta S = 2,3n \lg \frac{T_2}{T_1} + nb(T_2 - T_1) + \frac{nc}{2}(T_2^2 - T_1^2) + 2,3nR \lg \frac{p_2}{p_1}. \quad (\text{III.19})$$

Agar $T = \text{const}$ da hajm va bosim o'zgarsa, $V_1 \rightarrow V_2$, $p_1 \rightarrow p_2$;

$$\Delta S = 2,3nC_v \lg \frac{p_2 V_2^\gamma}{p_1 V_1^\gamma}. \quad (\text{III.20})$$

Agar $T = \text{const}$ va $p = \text{const}$ da V_1 va V_2 hajmdagi ideal gazlar diffuziyalanib, hajm $V = V_1 + V_2$ gacha kengaysa:

$$R \left(n_1 \lg \frac{V}{V_2} + n_2 \lg \frac{V}{V_1} \right) \cdot \Delta S \quad (\text{III.21})$$

yoki

$$\Delta S = -2,3R(n_1 + n_2)[N_1 \lg N_1 + N_2 \lg N_2], \quad (\text{III.22})$$

bunda: n_1 , n_2 — gazlarning mol soni; N_1 , N_2 — molar qismlari.

Izotermik potentsiallar (F , G). Gelmgols funksiyasi.

Jarayonning yo'nalishi va termodinamik muvozanat shartini izotermik-izoxorik ($T = \text{const}$, $V = \text{const}$) jarayonlarda Gelmgols funksiyasi (F) ning o'zgarishi ko'rsatadi:

$$F = U - TS. \quad (\text{III.23})$$

Qaytar jarayonda bajarilgan maksimal ish (A_{max}) Gelmgols funksiyasining kamayishiga teng:

$$A_{\text{max}} = -\Delta F. \quad (\text{III.24})$$

Qaytar jarayonda F o'zgarmaydi ($F_1 = F_2$). Qaytmas jarayon $F_1 > F_2$ potensialning kamayishi tomoniga boradi:

$$\Delta F \leq 0. \quad (\text{III.25})$$

«=»alohati qaytar va «<» alohati qaytmas jarayonga mansub. Muvozanat holatda F minimum qiymat bo'ladi:

$$dF = 0, \quad d^2F > 0. \quad (\text{III.26})$$

$$F = U - TS; \quad dF = dU - TdS - SdT. \quad (\text{III.27})$$

Agar dU qiymati (III.7) tenglamadan $dU = TdS - pdv$ ga qo'yilsa:

$$dF = -SdT - pdV$$

va

$$\left(\frac{dF}{dT}\right)_V = -S; \left(\frac{dF}{dV}\right)_T = -p. \quad (\text{III.28})$$

n — mol ideal gaz izotermik ravishda V_1 dan V_2 hajmgacha kengayganda va $T = \text{const}$ bo'lganda:

$$dF = -pdV = -\frac{RT}{V} dV \quad (\text{III.29})$$

$$\Delta F = 2,3nRT \lg \frac{V_2}{V_1} + 2,3nRT \lg \frac{p_1}{p_2}. \quad (\text{III.30})$$

F standart qiymatini (ΔF_{298}°) standart kattaliklardan hisoblash:

$$\Delta F_{298}^0 = \Delta U_{298}^0 - T\Delta S_{298}^0 \quad (\text{III.31})$$

$$\Delta U_{298}^0 = \left(\sum n \Delta U_{298}^0 \right)_{mahs.} - \left(\sum n \Delta U_{298}^0 \right)_{d.m.}$$

$$\Delta S_{298}^0 = \left(\sum n \Delta S_{298}^0 \right)_{mahs.} - \left(\sum n \Delta S_{298}^0 \right)_{d.m.}$$

bunda: *mahs* — mahsulot; *d.m.* — dastlabki moddalar.

Gibbs funksiyasi (potensial).

Izotermik-izobarik jarayonlarda ($T = \text{const}$ va $p = \text{const}$) jarayonning yo'nalishi va muvozanat shartini Gibbs funksiyasi (G) ning o'zgarishi ko'rsatadi:

$$G = U - TS + pV = F + pV = H - TS. \quad (\text{III.32})$$

Izotermik-izobarik ravishda boradigan qaytar jarayonda bajarilgan maksimal ish A_{max} :

$$\text{jarayonda } A_{\text{max}} = -\Delta G \quad (\text{III.33})$$

$$\Delta G \leq 0 \quad (\text{III.34})$$

bo'ladi.

«=» ishorasi qaytar va «<» ishorasi qaytmas jarayonga mansub, ya'ni qaytar jarayonda G o'zgarmaydi ($G_1 = G_2$) va qaytmas jarayonda kamayadi ($G_1 > G_2$).

G — minimum qiymatida muvozanat qaror topadi:

$$dG = 0; \quad d^2 G > 0. \quad (\text{III.35})$$

$$G = U - TS + p dV; \quad dG = dU - T dS - S dT + p dV + V dp.$$

dU ning qiymati (III.7) tenglamadan $dU = T dS - p dV$ (III.36) olib qo'yilsa:

$$dG = - S dT + p dV.$$

Bu tenglamadan:

$$\left(\frac{d \Delta G}{dp} \right)_T = V; \quad (\text{III.36})$$

$$\left(\frac{d \Delta G}{dT} \right)_p = -S \quad (\text{III.37})$$

va

$$dG = - S dT + V dP = S dT' + \frac{RT dp}{p}. \quad (\text{III.38})$$

$$\Delta G = 2,3nRT \lg \frac{P_2}{P_1}. \quad (\text{III.39})$$

Gibbs energiyasining standart qiymati (ΔG_{298}^0) ni standart kattaliklardan hisoblash:

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T \Delta S_{298}^0 \quad (\text{III.40})$$

$$\Delta H_{298}^0 = \left(\sum n \Delta H_{298}^0 \right)_M - \left(\sum n \Delta H_{298}^0 \right)_G$$

$$\Delta S_{298}^0 = \left(\sum n \Delta S_{298}^0 \right) - \left(\sum n \Delta S_{298}^0 \right).$$

Kimyoviy potensial (μ). Kimyoviy potensial moddalarning fazalar bo'yicha taqsimlanishini ko'rsatadi. i - moddaning kimyoviy potentsiali μ_i :

$$\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,V} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p} \quad (\text{III.41})$$

$$dN = RT d \ln p; \mu = \mu_{298}^0 + RT \cdot \ln p. \quad (\text{III.42})$$

$$\sum \mu_i dn_i = 0. \quad (\text{III.43})$$

Bu tenglama izotermik jarayonlarda moddalarning fazalar bo'yicha taqsimlanishining muvozanat shartidir. Demak, jarayon har qaysi moddaning fazadagi kimyoviy potentsiali tenglashishi tomon boradi va ularning fazalar bo'ylab kimyoviy potentsiallari tenglashganda muvozanat qaror topadi.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Turg'un bosimda 1 kmol kaliy bromid 300 dan 400 K gacha isitilganda entropiya qanchaga o'zgaradi? Qattiq holdagi kaliy bromidning solishtirma issiqlik sig'imi harorat bilan quyidagi tenglamaga muvofiq o'zgaradi:

$$c_p = 40,4 \cdot 10^{-2} + 12,8 \cdot 10^{-3} T \text{ J/g} \cdot \text{grad}.$$

Y e c h i s h . Bu holda entropiyaning o'zgarishi (III. 11) tenglamaga muvofiq:

$$\Delta S = n \int_{T_1}^{T_2} C_p \frac{dT}{T}.$$

Masala shartiga muvofiq $n = 1$. $M_{\text{KBr}} = 39 + 80 = 119$.

1 kmol KBr uchun molar issiqlik sig'imi $C_p = c_p \cdot M = (40,4 \cdot 10^{-2} + 12,8 \cdot 10^{-3} T) 119 \cdot 10^3$.

Demak,

$$\Delta S = \int_{300}^{400} \left(\frac{(40,4 \cdot 10^{-2} + 12,8 \cdot 10^{-3} T) 119 \cdot 10^{-3} \cdot dT}{T} \right) =$$

$$= 119 \cdot 10^3 \int_{300}^{400} \left(\frac{40,4 \cdot 10^{-2} dT}{T} + 12,8 \cdot 10^{-3} dT \right) =$$

$$= 119 \left(2,3 \cdot 404 \lg \frac{400}{300} + 12,8 (400 - 300) \right) = 248.500 \text{ J/kmol} \cdot \text{grad}.$$

2. 2 mol metan turg'un haroratda, $p_1 = 104,3 \cdot 10^5 \text{ N/m}^2$ dan $p_2 = 1,013 \cdot 10^5 \text{ N/m}^2$ gacha bosimda kengayganda entropiyaning o'zgarishini aniqlang.

Y e c h i s h . (III.17) ga muvofiq harorat turg'un bo'lganida:

$$\Delta S = -2,3nR \lg \frac{p_2}{p_1} = 2,3nR \lg \frac{p_1}{p_2}.$$

Demak:

$$\Delta S = 2 \cdot 2,3 \cdot 8,3141 \cdot \lg \frac{104,3 \cdot 10^5}{1,013 \cdot 10^3} = 76,4 \text{ J/mol} \cdot \text{grad}.$$

3. $1,013 \cdot 10^3 \text{ N/m}^2$ bosimda 2 g suv 0°C dan 150°C gacha isitilganda entropiyaning o'zgarishini aniqlang. Suvning bug'lanish yashirin issiqligi $\Delta H = 2,255 \text{ kJ/g}$. Bug'ning issiqlik sig'imi haroratga bog'liq ravishda quyidagicha o'zgaradi:

$$C_p = 30,13 + 11,3 \cdot 10^{-3} T, \text{ J/mol} \cdot \text{grad}.$$

Suvning issiqlik sig'imi turg'un deb faraz qilinsin va qiymat $C_p = 75,30 \text{ J/kmol} \cdot \text{grad}$ ga teng bo'lsin.

Y e c h i s h . Bu jarayon uch bosqichdan iborat:

- 1) suyuq suvning 0° dan 100°C gacha isitilishi;
- 2) 100°C da suvning bug'ga aylanishi;
- 3) bug'ning 100°C dan 150°C gacha isishi.

Umumiy entropiya shu bosqichlardagi entropiya o'zgarishi yig'indisiga teng:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3.$$

a) birinchi bosqichdagi entropiya o'zgarishi ($C_p = \text{const}$ da) (III.12) tenglamaga muvofiq:

$$\Delta S = 2,3nC_p \lg \frac{T_2}{T_1} = 2,3 \frac{2}{18} \cdot 75,30 \lg \frac{373}{273} = 2,61 \text{ J/mol} \cdot \text{grad};$$

b) ikkinchi bosqichda entropiyaning o'zgarishi (III.10) tenglamaga muvofiq:

$$\Delta S = \frac{n \cdot \Delta H}{T} = \frac{2}{18} \cdot \frac{2,55 \cdot 10^3}{373};$$

d) uchinchi bosqichda entropiyaning o'zgarishi (III.13) tenglamaga muvofiq:

$$\begin{aligned} \Delta S &= 2,3n \int_{373}^{423} \frac{C_p dT}{T} = \frac{2,3 \cdot 2}{18} \int_{373}^{423} \frac{(30,13 + 11,3 \cdot 10^{-3})}{T} dT = \\ &= \frac{2,3 \cdot 2}{18} \lg \frac{423}{373} + \frac{2,3 \cdot 2}{18} 11,3 \cdot 10^{-3} (423 - 373) = 0,49 \text{ J/mol} \cdot \text{grad} \end{aligned}$$

va

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 2,61 + 12,09 + 0,49 = 15,19 \text{ J/mol} \cdot \text{grad}.$$

4. Izotermik ravishda 1 mol azot va 1 mol kislorod o'zaro aralashtirilgan. Gazlarning bosimi bir xil bo'lsin. Ikkala gaz ham ideal gaz qonunlariga bo'ysunadi, deb faraz qilinganida entropiya o'zgarishini aniqlang.

Y e c h i s h . Ikkala gaz ham bir xil haroratga, bosim va hajmga bo'lganligidan gazlar aralashganda umumiy hajm 2 marta ko'payadi va (III.20 va 21) tenglamaga muvofiq:

$$\Delta S = -2,3R \left(n_1 \lg \frac{V}{V_1} + n_2 \lg \frac{V}{V_2} \right).$$

Tenglama shartiga muvofiq $V = V_1 + V_2$ va, demak,

$$\frac{V}{V_1} = 2; \frac{V}{V_2} = 2$$

$$\Delta S = 2,3 \cdot 8,314 (1 \cdot \lg 2 + 1 \cdot \lg 2) = 11,5 \text{ J/mol} \cdot \text{grad}.$$

5. $T_{\text{ar}} = 293 \text{ K}$ dagi 1 mol argon va $T_{\text{N}_2} = 323 \text{ K}$ haroratdagi 2 mol azot aralashtirilgan, moddalarning dastlabki bosimi va aralashma bosimi bir xil. Argon va azotning molar issiqlik sig'implari mos ravishda $C_{r,\text{Ar}} = 20,8 \text{ J/mol}$. $C_{p,\text{N}_2} = 29,4 \text{ J/mol}$. Aralashtirish jarayonida entropiyaning o'zgarishini aniqlang.

Y e c h i s h . Gazlar aralashishi natijasida gazlarning harorati va bosimi o'zgaryapti(kamaymoqda). Demak, entropiyaning umumiy o'zgarishi ikkala gazning harorati va bosimi o'zgarishi natijasida entropiyalarining o'zgarishi yig'indisiga teng:

$$\Delta S = \left(\Delta S_{\text{Ar}} + \Delta S_{\text{N}_2} \right)_T + \left(\Delta S_{\text{Ar}} + \Delta S_{\text{N}_2} \right)_p.$$

Bosim o'zgarmagandan $(\Delta S_{Ar} + \Delta S_{N_2})_p = 0$. Harorat o'zgarishi natijasida entropiyaning o'zgarishini (III. 12) tenglama ifoda qiladi:

$$\Delta S = 2,3 \cdot n C_p \lg \frac{T}{T_1}$$

va

$$\Delta S = (\Delta S_{Ar} + \Delta S_{N_2})_T = 2,3 \cdot 20,8 \lg \frac{T}{T_{Ar}} + 2,3 \cdot 2 \cdot 29,4 \lg \frac{T}{T_{N_2}}.$$

T aralashma harorati quyidagi balans tenglamadan aniqlanadi:

$$\begin{aligned} n_{Ar} C_{p_{Ar}} (T - T_{Ar}) &= n_{N_2} \cdot C_{p_{N_2}} (T_{N_2} - T) = 1 \cdot 20,8 (T - 293) = \\ &= 2 \cdot 29,4 (323 - T). \end{aligned}$$

Bu tenglama T ga nisbatan yechilsa, $T = 315$ K. Agar T ning bu qiymati yuqoridagi tenglamaga qo'yilsa:

$$\begin{aligned} \Delta S &= (\Delta S_{Ar} + \Delta S_{N_2}) = 20,8 \cdot 2,3 \lg \frac{315}{293} + 2 \cdot 29,4 \cdot 2,3 \lg \frac{315}{323} = \\ &= 1,594 - 1,504 = 0,033 \text{ J/mol} \cdot \text{grad}. \end{aligned}$$

6. Turg'un haroratda ($T = \text{const}$), 2 atm bosim ostida turgan 2 m^3 hajmdagi 1 mol gaz 4 m^3 gacha kengayganida entropiyaning o'zgarishini aniqlang. $C_p = 20,8 \text{ J/mol} \cdot \text{grad}$.

Yechish. Hajm 2 marta kengayganida bosim 2 marta kamaygan, demak, kengaygan gaz 1 atm bosim ostida (III. 20) tenglamaga muvofiq:

$$\Delta S = 2,3 n C_v \lg \frac{P_2 V_2^\gamma}{P_1 V_1^\gamma}.$$

C_v va γ ni aniqlaymiz:

$$C_p = C_v + R; C_v = C_p - R = 20,8 - 8,314 = 12,486 \text{ J/mol} \cdot \text{grad}.$$

$$\gamma = \frac{C_p}{C_v} = \frac{20,8}{12,486} = 1,67.$$

Demak:

$$\begin{aligned} \Delta S &= 2,3 \cdot 1 \cdot 12,486 \lg \frac{1 \cdot 4^{1,67}}{2 \cdot 2^{1,67}} = 2,3 \cdot 1 \cdot 12,486 \lg \frac{2^{1,67}}{2} = \\ &= 2,3 \cdot 1 \cdot 12,486 \cdot 3,4 = 42,4524 \text{ J/mol} \cdot \text{grad} . \end{aligned}$$

7. 1 kmol ideal gaz 298 K da 1 m³ dan 10 m³ hajmgacha kengaygan. Gazning bajargan ishini, Gelmgols va Gibbs funksiyalarining o'zgarishini aniqlang.

Yechish. ΔF va ΔG ning o'zgarishi (III.30) va (III.39) tenglamaga muvofiq:

$$\Delta F = 2,3 \cdot nRT \lg \frac{V_2}{V_1} .$$

$$\Delta G = 2,3 \cdot nRT \lg \frac{P_2}{P_1} = 2,3 \cdot nRT \lg \frac{V_2}{V_1} .$$

Demak:

$$\Delta F = -2,3 \cdot 1 \cdot 8,314 \cdot 10 \cdot 298 \lg \frac{10}{1} = -5,702 \cdot 10^3 \text{ J} .$$

$$\Delta G = 2,3 \cdot 1 \cdot 8,314 \cdot 298 \lg \frac{1}{10} = -5,702 \cdot 10^3 \text{ J} .$$

(III.24) va (III.33) tenglamalarga muvofiq $A_{\max}$:

$$A_{\max} = \Delta F = -\Delta G = 5,702 \cdot 10^3 \text{ J} .$$

8. 291 K da 1 mol suyuq toluol $1,013 \cdot 10^5$ bosimdan $10,13 \cdot 10^5$ N/m² ga siqilgan. Suyuqlikning siqilishini e'tiborga olmang

($V = \text{const}$). Gibbs funksiyasining o'zgarishini aniqlang. Toluolning zichligi $d = 867 \text{ kg/m}^3$ ga teng. Molekular og'irligi 92,14.

Yechish. (III.36) tenglamaga muvofiq:

$$dG = -SdT + Vdp$$

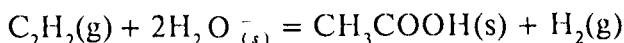
va T , V turg'un bo'lganda:

$$\Delta G = V(p_2 - p_1) = \frac{92,14}{867} \cdot (10,13 \cdot 10^5 - 1,013 \cdot 10^5) = 96,99 \approx 97 \text{ J},$$

tenglamadan V qiymati quyidagicha aniqlanadi:

$$d = \frac{m}{V} \text{ va } V = \frac{M}{d} = \frac{92,14}{867}.$$

9. Quyidagi reaksiya uchun:



$$\Delta H_{298}^0, \Delta U_{298}^0, \Delta A_{298}^0, \Delta G_{298}^0 \text{ va } \Delta S_{298}^0$$

ning standart qiymatlarini aniqlang. Kerakli kattaliklar quyidagi jadvalda berilgan.

Modda	$\Delta H_{298}^0, \text{ J/mol}$	$\Delta S_{298}^0, \text{ J/mol} \cdot \text{grad}$
$\text{C}_2\text{H}_{2(\text{gaz})}$	$226,75 \cdot 10^3$	200,8
$\text{H}_2\text{O}_{(\text{suyuq})}$	$-285,84 \cdot 10^3$	69,96
$\text{CH}_3\text{COOH}_{(\text{suyuq})}$	$-484,9 \cdot 10^3$	199,8
$\text{H}_{2(\text{gaz})}$	0	130,6

Yechish. (I.II) tenglamaga muvofiq:

$$H = U + pV = U + \Delta nRT.$$

Stexiometrik koeffitsiyentlarni hisoblaganda faqat gazsimon moddalargina e'tiborga olinadi:

$$\Delta n = n_{\text{H}_2} - n_{\text{C}_2\text{H}_2} = 1 - 1 = 0.$$

Demak:

$$\Delta n R = 0,$$

$$\Delta H_{298}^0 = \Delta U_{298}^0.$$

(III.40) tenglamaga muvofiq:

$$\begin{aligned} \Delta H_{298}^0 &= \left(\Delta H_{298, \text{CH}_3\text{COOH}}^0 + \Delta H_{298, \text{H}_2}^0 \right) - \left(\Delta H_{298, \text{C}_2\text{H}_2}^0 + \Delta H_{298, \text{H}_2\text{O}}^0 \right) = \\ &= \left(-484,910^3 + 0 \right) - \left(226,75 \cdot 10^3 - 2 \cdot 285,84 \cdot 10^3 \right) = 139,47 \cdot 10^3 \text{ J/mol}, \end{aligned}$$

$$\Delta S_{298}^0 = (159,8 + 130,6) - (2 \cdot 69,96 + 200,8) = -50,26 \text{ J/mol} \cdot \text{grad},$$

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T \Delta S_{298}^0 = 139,47 \cdot 10^3 - 298 \cdot 50,26 = 154,96 \text{ kJ/mol},$$

$$A_{298}^0 = -\Delta G_{298}^0 = +154,96 \text{ kJ}.$$

10. $0,5\text{N}_2 + 1,5\text{H}_2 = \text{NH}_3$ reaksiyasi uchun 400 K da ΔG ning o'zgarish qiymatini aniqlang. $\Delta G_{298}^0 = 16,496 \cdot 10^3 \text{ J/mol}$ ga teng. $\Delta S_{298, \text{NH}_3}^0 = 192,50$, $\Delta S_{298, \text{H}_2}^0 = 191,50$, $\Delta S_{298, \text{N}_2}^0 = 130,6 \text{ J/mol}$. $DS = \text{const}$ deb qabul qiling.

Y e c h i s h . (III.36) tenglamaga muvofiq:

$$dG = -SdT + Vdp.$$

$p = \text{const}$ va $dp = 0$ bo'lganligidan:

$$dG = -SdT \text{ va } \Delta G_T = \Delta G_{298}^0 - \int_{298}^T \Delta S_{298}^0 dT,$$

$$\Delta G_T = \Delta G_{298}^0 - \Delta S_{298}^0 (T - 298),$$

$$\Delta S^0 = \Delta S_{\text{NH}_3} - 0,5S_{\text{N}_2}^0 - 1,5S_{\text{H}_2}^0 = 192,5 - (0,5 \cdot 191,5 + 1,5 \cdot 130,6) = 99,15.$$

Demak:

$$\begin{aligned}\Delta G_{400} &= 16,496 \cdot 10^3 - [99,15(400 - 298)] = \\ &= 16,496 \cdot 10^3 - 99,15 \cdot 102 = 6,383 \text{ J/mol} \cdot \text{grad}.\end{aligned}$$

MASALALAR

1. 10 g azot N_2 ni: a) turg'un bosim, b) turg'un hajmda 0° dan 100°C gacha qizdirilganda entropiyaning o'zgarishi qanchaga teng? Azotning issiqlik sig'imi $C_p = 6,954 \text{ kal/grad}$ ga teng bo'lib, turg'un, haroratga bog'liq emas, deb faraz qiling.

2. 2 g suv 0° dan 150° gacha $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda bug'langanda entropiya qanchaga o'zgaradi? Suvning yashirin bug'lanish issiqligi $\Delta H = 2,255 \text{ kJ/g}$, suyuq suvning molar izobarik issiqlik sig'imi turg'un bo'lib, $C_p = 75,30 \text{ J/mol} \cdot \text{grad}$ ga teng, suv bug'ining izobarik issiqlik sig'imi harorat bilan quyidagicha o'zgaradi: $C_p = 30,13 + 11,3 \cdot 10^{-3} T \text{ J/mol} \cdot \text{grad}$.

3. 10 g brom benzol bug'langanda entropiyaning o'zgarishi qanchaga teng bo'ladi? Brom benzol $429,8 \text{ K}$ da qaynaydi, yashirin bug'lanish issiqligi $\Delta H = 241,9 \cdot 10^3 \text{ J/kg}$ ga teng.

4. 870 K da kumush xloridning entropiyasini aniqlang. Hamma harorat chegarasida $S_{298}^0 = 219,02 \text{ J/mol} \cdot \text{grad}$ ga teng, AgCl ning suyuqlanish harorati 728 K . Qattiq kumush xloridning $C_p = 66,94 \text{ J/mol}$, suyuqlanish yashirin issiqligi $\Delta H = 12886,7 \text{ J/mol}$ ga teng. Qattiq AgCl ning $S_{298}^0 = 90,07 \text{ J/mol}$, suyuq kumush xloridning issiqlik sig'imi $C_p = 62,26 + 4,18 T - 11,30 \cdot 10^5 T^2$.

5. 1 g mol kadmiy sulfid 100°C dan 0°C gacha isitilganda entropiya qanchaga o'zgaradi? Kadmiy sulfidning izobarik molar issiqlik sig'imi harorat bilan quyidagi tenglamaga muvofiq o'zgaradi:

$$C_p = 54,0 + 3,8 \cdot 10^{-3} T, \text{ J/mol} \cdot \text{grad}.$$

6. 10 g kripton izotermik ravishda hajmi $0,05 \text{ m}^3$ dan $0,2 \text{ m}^3$ gacha kengayganda va bosimi $1,013 \cdot 10^5 \text{ N/m}^2$ dan $0,2133 \cdot 10^5 \text{ N/m}^2$ gacha kamayganda entropiyaning o'zgarishini aniqlang.

7. 1 kg mis suyuqlanganda entropiyaning o'zgarishi qanchaga teng? Misning suyuqlanish harorati 1083°C ga, solishtirma yashirin suyuqlanish issiqligi $41,6 \text{ kal/g} \cdot \text{grad}$ ga teng.

8. 1 g atom kumush 25°C dan 225°C gacha qizdirilganda entropiyaning o'zgarishini aniqlang. Misning gramm-atom izobarik issiqlik sig'imi harorat bilan quyidagicha o'zgaradi:

$$C_p = 5,593 + 1,49 \cdot 10^{-3} T, \text{ kal/g-atom} \cdot \text{grad}.$$

9. $0,001 \text{ m}^3$ vodorod $0,0005 \text{ m}^3$ metan bilan aralashtirilganda entropiyaning o'zgarishini aniqlang. Aralashma hosil qiluvchi gazlar aralashishdan oldin 25°C da va $0,012 \cdot 10^5 \text{ N/m}^2$ bosimga ega bo'lgan.

10. $0,02 \text{ m}^3$ hajmni ishg'ol qilgan 1 mol gaz izotermik kengayganda entropiyaning o'zgarishi $32,28 \text{ J/mol} \cdot \text{grad}$ ga teng bo'lgan. Gaz kengaygandan so'ng uning hajmi qanchaga teng bo'ladi?

11. CO ning 506 K da va 2 atm bosimdagi molar entropiyasini aniqlang. CO ning standart entropiyasi $S_{298}^0 = 47,301 \text{ kal/mol} \cdot \text{grad}$ ga teng. Izobarik molar issiqlik sig'imi harorat bilan quyidagi tenglamaga muvofiq o'zgaradi:

$$C_p = 6,342 + 1,836 \cdot 10^{-3} T.$$

12. $T = 293 \text{ K}$ va $p_{\text{Ar}} = 1,0133 \cdot 10^5 \text{ N/m}^2$ 1 mol argon, $T_{\text{N}_2} = 323 \text{ K}$ va $p_{\text{N}_2} = 1,0133 \cdot 10^5 \text{ N/m}^2$ dagi azot bilan aralashtirilgan. Aralashmaning bosimi $p = 1,0133 \cdot 10^5 \text{ N/m}^2$ ga teng. Ularning izobarik issiqlik sig'implari bayon etilgan harorat va bosimda turg'un bo'lib:

$$C_{V,\text{Ar}} = 20,935 \text{ J/mol} \cdot \text{grad}.$$

$$C_{V,\text{N}_2} = 12,561 \text{ J/mol} \cdot \text{grad}.$$

Aralashish jarayonida entropiyaning o'zgarishi qanchaga teng?

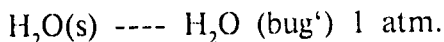
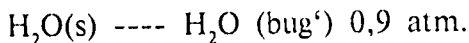
13. 2 mol CH_3OH metil spirti 25°C dan 100°C gacha isitilganda entropiyaning o'zgarishini aniqlang. Metanolning qaynash harorati $T_q = 61,7^\circ\text{C}$. Solishtirma yashirin bug'lanish issiqligi $l = 81,50 \text{ J/mol} \cdot \text{grad}$, metanol bug'ining molar issiqlik sig'imi:

$$C_p = 15,28 + 105,2 \cdot 10^{-3} T - 31,04 \cdot 10^{-5} T^2 \text{ J/mol} \cdot \text{grad}.$$

14. 7 g azot 27°C da 0,5 dan 3 atmosferagacha siqilganda Gelmhols funksiyasining o'zgarishini aniqlang.

15. Quyidagi jarayonlarda 25°C da izoxorik potensial ΔF ning o'zgarishini aniqlang.

$$\Delta F_{298}^0 = 2055 \text{ kal/mol ga teng.}$$



16. Quyidagi ma'lumotlardan:

$$\Delta H_{298}^0(\text{ZnO}) = - 8317 \text{ kal/mol;}$$

$$\Delta H_{298}^0(\text{CO}) = - 26416 \text{ kal/mol;}$$

$$\Delta H_{298}^0(\text{CO}_2) = -94052 \text{ kal/mol};$$

$$\Delta H_{298}^0(\text{Zn}) = 0;$$

$$\Delta S_{298}^0 \text{ZnO} = 10,5 \text{ kal/mol} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{CO}) = 47,301 \text{ kal/mol} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{CO}_2) = 51,06 \text{ kal/mol} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{Zn}) = 9,95 \text{ kal/mol} \cdot \text{grad}$$

foydalanib, 25°C da quyidagi reaksiyada $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ Gelmgols funksiyasining standart qiymatini aniqlang.

17. Quyidagi ma'lumotlardan foydalanib:

$$\Delta H_{298}^0(\text{Cd}) = 0;$$

$$\Delta H_{298}^0(\text{AgCl}) = -126,8 \text{ kJ/mol};$$

$$\Delta H_{298}^0(\text{Ag}) = 0;$$

$$\Delta H_{298}^0(\text{CdCl}_2) = -398,0 \text{ kJ/mol};$$

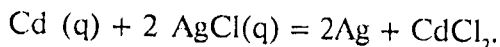
$$\Delta S_{298}^0(\text{Cd}) = 51,76 \text{ J/g-atom} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{AgCl}) = 66,07 \text{ J/mol} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{Ag}) = 42,69 \text{ J/g-atom} \cdot \text{grad};$$

$$\Delta S_{298}^0(\text{CdCl}_2) = 115,3 \text{ J/mol} \cdot \text{grad}.$$

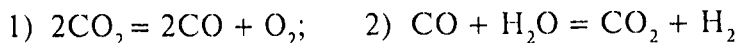
Izobarik potensial ΔG_{298}^0 ning quyidagi reaksiyada o'zgarishini aniqlang:



18. 25°C da 1 g-atom grafitning entropiyasi 5,72 J/grad, 1 g-atom olmosning entropiyasi 2,38 J/grad ga teng. Olmosning yonish issiqligi grafitning yonish issiqligidan 752 J ga ko'p. Izotermik

ravishda grafitning olmosga o'tishida izobarik potensialning o'zgarishini aniqlang.

19. Quyidagi reaksiyalar:



uchun 700 K da ΔG_{700}^0 qiymatini aniqlang.

$$\Delta H_{298}^0(\text{CO}_2) = -398,51 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298}^0(\text{CO}) = -578 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298}^0(\text{H}_2\text{O}) = -241,84 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298}^0(\text{H}_2) = 0;$$

$$C_p(\text{H}_2\text{O}) = 30,0 + 10,71 \cdot 10^{-3} T + 0,33 \cdot 10^5 T^2;$$

$$C_p(\text{CO}_2) = 28,4 + 4,101 \cdot 10^{-3} T - 0,46 \cdot 10^5 T^2;$$

$$C_p(\text{CO}) = 28,41 + 4,10 \cdot 10^{-3} T - 0,46 \cdot 10^5 T^2;$$

$$C_p(\text{O}_2) = 31,46 + 3,30 \cdot 10^{-3} T - 3,77 \cdot 10^5 T^2;$$

$$C_p(\text{H}_2) = 27,28 + 3,26 \cdot 10^{-3} T + 0,502 \cdot 10^5 T^2.$$

20. $\text{FeCO}_3 = \text{FeO} + \text{CO}_2$ reaksiya uchun:

$$\Delta H_T^0 = 17597 + 30,02 \cdot T - 11,54 \cdot T \cdot \ln T + 11,578 \cdot 10^{-3} T^2 - 1,3 \cdot 10^5 T^{-1} \text{ teng } \Delta H_{500}^0 \text{ va } \Delta S_{500}^0 \text{ dagi qiymatlarni aniqlang.}$$

21. $\text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O(s)} + \text{CO}_2$ reaksiyada CH_4 10 atm, kislorod 5 atm va CO_2 20 atm da olingan. ΔF_{298}^0 ning qiymatini aniqlang.

22. 1 mol suyuq benzolning qaynash harorati $80,1^{\circ}\text{C}$ da $p_1 = 1,013 \cdot 10^5 \text{ N/m}^2$ bosimdan $p_2 = 9,11 \cdot 10^5 \text{ N/m}^2$ bosimdagi bug'ga aylantirish jarayonida izobarik potensialning o'zgarishini aniqlang.

23. 1 mol ideal gaz izotermik ravishda 773 K da $p_1 = 5,05 \cdot 10^3$ dan $1,013 \cdot 10^4 \text{ N/m}^2$ gacha siqilgan. ΔU , ΔH , ΔS , ΔF , ΔG larning qiymatini aniqlang.

24. $298,2 \text{ K}$ harorat va $5,063 \cdot 10^5 \text{ Pa}$ bosimda $1 \cdot 10^{-3} \text{ m}^3$ kislorod, adiabatik ravishda $1,043 \cdot 10^5 \text{ Pa}$ ga qadar kengaytirilgan. $C_{p, \text{O}_2} = 20,63 \text{ J/mol} \cdot \text{grad}$, $298,2 \text{ K}$ harorat va $1,013 \cdot 10^5 \text{ Pa}$ da molar entropiyasi 206 J/mol ga teng. U , H , S , A , G larni va oxirgi V , T ni aniqlang.

KO'P VARIANTLI MASALALAR

1. 1 mol A (gaz) 1-holatdan ($T_1 = 298 \text{ K}$, $p_1 = 1,013 \cdot 10^5 \text{ Pa}$) dan 2-holatga (T_2, p_2) ga o'tganda ΔU , ΔH , ΔS , ΔF , ΔG larning o'zgarishini aniqlang. Kerakli ma'lumotlarni ilova (ma'lumot-noma)dan oling.

№	$A(\text{gaz})$	$p_2 \cdot 10^{-2}, \text{ Pa}$	$T_2, \text{ K}$
1	H_2	1,33	250
2	H_2O	13,3	350
3	CH_4	1,33	500
4	CH_4	13,3	550
5	CO	133	600
6	CO_2	1330	650
7	CO_2	1,3	700
8	CO_2	13,33	750
9	C_2H_6	133,3	800

10	C_2H_6	1333	850
11	N_2	1,33	900
12	N_2	13,33	950
13	O_2	133,3	1000
14	O_2	1333	250
15	O_2	1,33	350
16	F_2	13,33	400
17	Cl_2	1333	500
18	Cl_2	1,333	550

2. 25°C da boradigan kimyoviy reaksiyaning standart hosil bo'lish issiqligi ΔH_{298}^0 dan va entropiyaning mutlaq qiymati SO gazidan foydalanib, izobarik potensialning standart qiymati ΔG_{298}^0 ni aniqlang. Kerakli ma'lumotlarni ilovadan oling (g—gaz, s—suyuqlik, q—qattiq holatni ko'rsatadi).

No	Reaksiya
1	$ZnO (q) + CO = Zn(q) + CO_2$
2	$ZnS (q) + H_2 = Zn(q) + H_2S$
3	$2CO_2 (g) = 2CO (g) + O_2$
4	$CO (g) + H_2O(s) = CO_2 + H_2$
5	$CO + 2H_2 = CH_3OH$
6	$2HIJ (g) = H_2 + J_2 (g)$
7	$NH_3NH_3 + HCl (g) = NH_4Cl(q)$
8	$H_2 + CO_2 = CO + H_2O (c)$
9	$CO_2 + 4H_2 = CH_4$
10	$2H_2O (s) = CH_4$
11	$SO_2 + Cl_2 = SOCl_2 (g)$
12	$CO + Cl_2 = COCl_2(g)$
13	$4HCl (g) + O_2 = 2H_2O (s) + 2 Cl_2$
14	$CH_3CHOH(g) + 2H_2 = 2CH_3OH (g)$
15	$CO + 3H_2 = CH_4 + H_2O (g)$
16	$H_2 + HCOOH = CH_3OH$

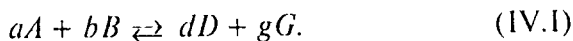
17	$4 \text{NH}_3 + \text{SO}_2 = 6 \text{H}_2\text{O (g)} + 4 \text{NO}$
18	$\text{CH(OH)}_2 = \text{CaO} + \text{H}_2\text{O (s)}$
19	$\text{PCl}_5(\text{g}) = \text{PCl}_3(\text{g}) + \text{Cl}_2$
20	$\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O (s)}$
21	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$
22	$\text{H}_2\text{S} + \text{COS (g)} = \text{H}_2\text{O(g)} + \text{CS}_2(\text{g})$
23	$\text{H}_2\text{S} + \text{COS (g)} = \text{H}_2\text{O (g)} + \text{CS}_2(\text{g})$
24	$\text{C}_6\text{H}_6(\text{g}) + 3\text{H}_2 = \text{C}_6\text{H}_{12}(\text{s})$
25	$\text{C}_6\text{H}_6(\text{s}) = \text{C}_2\text{H}_4 + \text{H}_2\text{O (g)}$
26	$\text{CH}_2 + 2\text{H}_2\text{S} = \text{CS}_2(\text{s}) + 4\text{H}_2$
27	$2 \text{AgNO}_3 = 2\text{Ag} + 2 \text{NO}_2 + \text{O}_2$
28	$4 \text{CO} + 2\text{SO}_2 = \text{S}_2(\text{q}) + 4 \text{CO}_2$
29	$2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O(g)} + \text{CO}_2$
30	$\text{MgCO}_3 = \text{MgO} + \text{CO}_2$

IV bob

KIMYOVIY MUVOZANAT

Muvozanat konstantasi. Qaytar reaksiyalarda bir xil sharoitda reaksiya bir vaqtning o'zida ikki tomonga boradi va muvozanat qaror topganda dastlabki moddalarning bir qismi o'zgarmasdan qoladi. Muvozanat qaror topgandagi konsentratsiya (parsial bosim)lar muvozanat konsentratsiya (parsial bosim)lari deyiladi. Reaksiya unumini muvozanat konstantasi (K) qiymati ko'rsatadi. Agar muvozanat konstantasi ma'lum bo'lsa, muvozanat holatidagi sistema tarkibini va aksincha, muvozanat holatidagi tarkibdan muvozanat konstantasini aniqlash mumkin.

Muvozanat konstantasi ideal sistemalar (o'ta suyultirilgan eritmalar va o'ta kichik bosimdagi aralashmalar) uchun konsentratsiya va bosim orqali, real sistemalar uchun termodinamik aktivlik va uchuvchanlik orqali ifodalanadi. Muvozanat konstantasi ifodasida kasr maxrajida mahsulotlar va suratda dastlabki moddalarga mansub kattaliklar bo'ladi. Masalan:



Reaksiya uchun:

$$K_c = \frac{C_A^d \cdot C_G^g}{C_A^a \cdot C_B^b}, \quad (\text{IV.2})$$

C_A, C_B, C_D, C_G — muvozanat molar konsentratsiyalaridir.

Muvozanat konstantasi molar qism (N) orqali ham ifoda qilinadi:

$$K_N = \frac{N_H^d \cdot N_G^g}{N_A^a \cdot N_B^b}, \quad (\text{IV.3})$$

$N_A, N_B, N_D, N_G - A, B, D, G$ moddalarning (muvozanatdagi) aralashmadagi molar qismlari.

i - komponentning molar qismi (N_i) quyidagicha aniqlanadi:

$$N_i = \frac{n_i}{\sum n_i}, \quad (\text{IV.4})$$

n_i — mol soni.

Gazlar aralashmalari uchun muvozanat parsial bosimlari orqali ifodalanadi:

$$K_p = \frac{P_D^d \cdot P_G^g}{P_A^a \cdot P_B^b}. \quad (\text{IV.5})$$

g — gazning parsial bosimini Dalton qonuni yordamida mol sonidan (n_i) foydalanib hisoblab aniqlash mumkin:

$$\frac{n_i}{\sum n_i} = \frac{P_i}{\sum P_i} \quad (\text{IV.6})$$

$$P_i = \frac{n_i}{\sum n_i} \cdot \sum P_i = \frac{n_i}{\sum n_i} P, \quad (\text{IV.7})$$

$\sum n_i$ — hamma moddalarning mollar soni yig'indisi,
 $P = \sum P_i$ — umumiy bosim.

Bu ifodalar o'rtasida quyidagicha bog'lanish bor:

$$K_p = K_c(RT)^{\Delta n} = K_n P^{\Delta n} \quad (\text{IV.8})$$

$$\Delta n = (d + g) - (a + b).$$

Agar $\Delta n = 0$ bo'lsa,

$$K_p = K_c = K_n.$$

Real sistemalarda muvozanat konstantasi moddalarning bir-biriga ta'siri (tortilishi)ni e'tiborga olgan konsentratsiya va bosim ifodasi bo'lgan termodinamik aktivlik (a) va uchuvchanlik (f) orqali ifodalanadi:

$$a = \gamma C; \quad f = \gamma P. \quad (\text{IV.9})$$

γ — termodinamik aktivlik koeffitsiyenti bo'lib, moddalarning bir-biriga tortilishini tavsiflovchi kattalikdir.

$$K_a = \frac{a_D^d a_G^g}{a_A^a \cdot a_B^b} \quad (\text{IV.10})$$

$$K_p = \frac{f_D^d f_G^g}{f_A^a \cdot f_B^b} \quad (\text{IV.11})$$

$$K_p = \frac{P_D^d P_G^g}{P_A^a \cdot P_B^b} \cdot \frac{\gamma_D^d \gamma_G^g}{\gamma_A^a \gamma_B^b} = K_p \cdot K_\gamma, \quad (\text{IV.12})$$

bunda

$$K_\gamma = \frac{\gamma_D^d \gamma_G^g}{\gamma_A^a \gamma_B^b}. \quad (\text{IV.13})$$

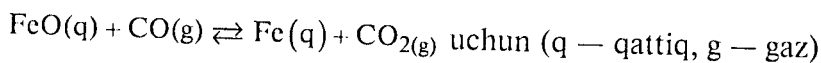
Uchuvchanlik (yoki aktivlik) koeffitsiyenti qiymati keltirilgan harorat (τ) va keltirilgan bosimda (π) ma'lumotnomalarda berilgan:

$$\tau = \frac{T}{T_K}; \quad \pi = \frac{P}{P_K}, \quad (\text{IV.14})$$

bunda: T, P — mutlaq harorat va bosim; T_k, P_k — kritik harorat va kritik bosim.

γ — qiymati turli gazlarning bir xil keltirilgan harorat va bosimda taxminan bir xil qiymatda bo'ladi. τ, π va γ ning qiymati ma'lumotnomalarda berilgan.

Geterogen sistemalarda faqat gazsimon moddalarninggina parsial bosimlari e'tiborga olinib, suyuq va qattiq holatdagi moddalarning bosimi ularning miqdoriga bog'liq bo'lmaganligidan, muvozanat konstantasi ifodasida ularning kattaliklari e'tiborga olinmaydi. Masalan,



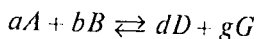
$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \quad (\text{IV.15})$$

bo'ladi.

Muvozanat konstantasining qiymati reaksiya uchun dastlab olingan moddalarning konsentratsiyasi(yoki bosimi)ga bog'liq bo'lmasdan, faqat haroratga bog'liq.

KIMYOVIY REAKSIYALAR IZOTERMASI

Ideal gazlar o'rtasida yoki ideal eritmada borayotgan



reaksiya uchun reaksiya izotermasi quyidagicha bo'ladi:

$$\Delta F = 2,3RT \left[\lg \frac{C_D^d C_G^g}{C_A^a C_B^b} - \lg K_c \right] \quad (\text{IV.16})$$

$$\Delta G = 2,3RT \left[\lg \frac{P_D^d P_G^g}{P_A^a P_B^b} - \lg K_p \right] \quad (\text{IV.17})$$

c, p — dastlabki olingan va hosil bo'lgan moddalarning molar konsentratsiyasi va parsial bosimi.

$\Delta F, \Delta G$ qiymatlariga qarab ma'lum reaksiyaning borish-bormasligini aniqlash mumkin. Agar $\Delta F < 0$; $\Delta G < 0$ bo'lsa, reaksiya to'g'ri tomonga (chapdan o'ngga) o'z-o'zicha boradi. Agar $\Delta F > 0$, $\Delta G > 0$ bo'lsa, reaksiya to'g'ri tomonga o'zicha bormaydi. Agar $\Delta F = 0$, $\Delta G = 0$ bo'lsa, sistema muvozanat holatda bo'ladi.

IV.1. REAKSIYANING MUVOZANAT KONSTANTASIGA HARORATNING TA'SIRI

Reaksiya muvozanat konstantasi qiymatining harorat bilan o'zgarishi (ta'siri) izoxorik va izobarik tenglamalarda ifodalangan:

$$-\frac{d \ln K_c}{dT} = \frac{\Delta U}{RT^2}; \quad \Delta U = -\frac{RT^2 d \ln K}{dT}; \quad (\text{IV.18})$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}; \quad \Delta H = -\frac{RT^2 d \ln K_p}{dT}.$$

Agar bu tenglamalar integrallansa (bunda issiqlik effekti harorat bilan o'zgarmas deb faraz qilinsa va bu faraz faqat haroratning kichik farqida mumkin), quyidagi hosil qilinadi:

$$\lg K_c = \frac{\Delta U}{2,3RT} + \text{const}, \quad \lg K_p = \frac{\Delta H}{2,3RT} + \text{const}. \quad (\text{IV.19})$$

Ikki harorat T_1, T_2 da:

$$\lg \frac{K_{c,2}}{K_{c,1}} = - \frac{\Delta U}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right), \quad (\text{IV.20})$$

$$\lg \frac{K_{p,2}}{K_{p,1}} = - \frac{\Delta H}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right). \quad (\text{IV.21})$$

Aniq hisoblarda issiqlik effektining haroratga bog‘liqligini e‘tiborga olish kerak. Bu bog‘lanish Kirxgof tenglamasida berilgan.

Kimyoviy reaksiyaning issiqlik effektini va muvozanat holatdagi tarkibini izoxora-izobara tenglamasidan foydalanib aniqlash mumkin:

$$\Delta H = \frac{RT^2 \ln K_p}{dT}. \quad (\text{IV.22})$$

Muvozanat konstantasining haroratga bog‘liq ravishda o‘zgarishi ma’lum bo‘lsa, reaksiyaning issiqlik effektini aniqlash mumkin.

IV.2. MUVOZANAT KONSTANTASI QIYMATINI NAZARIY ANIQLASH

Muvozanat konstantasi qiymatini standart izotermik potensiallardan (F°, G°) izoterma tenglamasidan foydalanib ham aniqlash mumkin.

Agar ideal gazlar orasida borayotgan reaksiyada parsial bosim 1 atm ga teng deb faraz qilinsa, ya’ni:

$P_A = P_B = P_D = P_G = 1$ atm yoki $C_A = C_B = C_D = C_G = 1$ kmol/m³ (m/l) bo‘lsa, izoterma (IV.14) va (IV.15) tenglamalaridan:

$$\Delta F = - 2,3RT \lg H_c; \quad \Delta G = - 2,3RT \lg K_p; \quad (\text{IV.23})$$

$$\Delta F_a = -2,3RT \lg K_a; \quad \Delta G_b = -2,3RT \lg K_p. \quad (\text{IV.24})$$

Bu tenglamalardan:

$$\lg K_c = -\frac{\Delta F}{2,3RT} \cdot \lg K_p = -\frac{\Delta G}{2,3RT}. \quad (\text{IV.25})$$

$\Delta G = \Delta H - T\Delta S$ bo'lganligidan:

$$\lg K_{p,T} = -\frac{\Delta H_T}{2,3RT} + \frac{\Delta S_T}{2,3R}, \quad (\text{IV.26})$$

$$\Delta H_T = \Delta H_{298}^0 + \int_{298}^T \Delta C_p dT, \quad (\text{IV.27})$$

$$\Delta S_T = \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p dT}{T}, \quad (\text{IV.28})$$

bu tenglamada:

$$\Delta C_p = (\sum \Delta C_p)_m - (\sum \Delta C_p)_d$$

$$\Delta H_{298}^0 = \left(\sum \Delta H_{298}^0 \right)_m - \left(\sum \Delta H_{298}^0 \right)_d$$

$$\Delta S_{298}^0 = \left(\sum \Delta S_{298}^0 \right)_m - \left(\sum \Delta S_{298}^0 \right)_d,$$

ΔH_{298}^0 — moddalar; m — mahsulot; d — dastlabki moddalar.

Bu tenglamalardan:

$$\Delta G_T = \Delta H_{298}^0 - \int_{298}^T \Delta C_p dT - T \int_{298}^T \frac{\Delta C_p dT}{T}$$

va

$$\lg K_{p,T} = -\frac{\Delta H_{298}^0}{nRT} + \frac{\Delta S_{298}^0}{2,3R} - \frac{1}{2,3RT} \int_{298}^T \Delta C_p dT + \frac{1}{2,3R} \int_{298}^T \frac{\Delta C_p dT}{T}. \quad (\text{IV.29})$$

Taxminiy hisoblarda $\Delta C_p = 0$ teng deb faraz qilinsa:

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R}.$$

Agar $C_p \neq f(T)$, ya'ni C_p lar turg'un deb faraz qilinsa:

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R} - \frac{\Delta C_p}{2,3RT} \left[(T-298) - T \lg \frac{T}{298} \right]. \quad (\text{IV.30})$$

Agar aniq hisoblash kerak bo'lsa, tenglamada C_p larning haroratga bog'lanishi hisobga olinadi.

(IV.28) tenglamani Temkin-Shvarsman usuli bilan yechish mumkin. (IV.29) tenglamani quyidagicha yozamiz:

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R} + \frac{J}{2,3R}, \quad (\text{IV.31})$$

bunda

$$J = \frac{1}{T} \int_{298}^T \Delta C_p dT + \int_{298}^T \frac{\Delta C_p dT}{T}. \quad (\text{IV.32})$$

C_p ning haroratga bog'lanishi (IV.28) tenglamaga qo'yilsa,

$$J = \Delta a M_o + \Delta b M + \Delta c M_2 + \Delta c M_{-2}, \quad (\text{IV.33})$$

M_o, M_1, M_2, M_{-2} lar haroratga bog'liq funksiya bo'lib, ularning qiymatlari ma'lumotnomalarda berilgan.

a, b, c lar $C_p = f(T)$ dagi turg'un koeffitsiyentlar.

Statistik usul. Statistik termodinamika usuli bilan turli termodinamik funksiyalarning mutlaq qiymatini hisoblab aniqlash

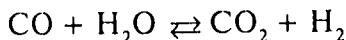
mumkin, demak, bu funksiyalar orqali muvozanat konstantasi qiymatini aniqlash mumkin. Muvozanat konstantasi termodinamik funksiya bilan quyidagicha bog'langandir:

$$R \ln K_p = - \left[\Delta \left(\frac{G^0 - H^0}{T} + \frac{\gamma H^0}{T} \right) \right].$$

ΔH^0 — 1 mol gazning mutlaq noldagi entalpiya o'zgarishi.
 $\frac{G^0 - H^0}{T}$ — keltirilgan izobar potentsial. $G^0 - H^0$ va ΔH^0 — turli moddalar uchun ma'lumotnomalarda berilgan.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Quyidagi reaksiyaning



1080 K dagi muvozanat konstantasi $K_c = 1$ ga teng. Reaksiya uchun dastlab 2 mol CO va 3 mol H_2O olingan, hamma moddalar gaz holida. Muvozanat holati tarkibini — moddalarning muvozanat konsentratsiyalarini mol foiz hisobida aniqlang.

Y e c h i s h . Muvozanat qaror topganda x mol CO_2 hosil bo'lgan deb faraz qilinsa, H_2 ning miqdori ham x mol ga teng. Demak, dastlabki moddalarning muvozanatdagi mol soni $n_{\text{CO}} = 2 - x$ va $n_{\text{H}_2\text{O}} = 3 - x$ ga teng. Bu qiymatlar muvozanat konstantasi tenglamasi ifodasiga (IV.2) qo'yilsa:

$$K = \frac{x_{\text{CO}_2} \cdot x_{\text{H}_2}}{n_{\text{CO}} \cdot n_{\text{H}_2\text{O}}} = \frac{x^2}{(2-x)(3-x)}$$

bu tenglamadan x aniqlanadi: $x = 1,2$. $\sum n_i = 5$ ga teng va muvozanat holati tarkibi mol foiz hisobida quyidagicha bo'ladi:

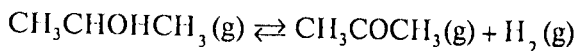
$$\text{CO}_2 = \frac{1,2 \cdot 100}{5} = 24\% ,$$

$$\text{H}_2 = \frac{1,2 \cdot 100}{5} = 24\% ,$$

$$\text{CO} = \frac{(2-1,2) \cdot 100}{5} = 16\% ,$$

$$\text{H}_2\text{O} = \frac{(3-1,2) \cdot 100}{5} = 36\% .$$

2. Gaz fazasida izopropil spirt degidratlanish (vodorodsizlanish) reaksiyasining

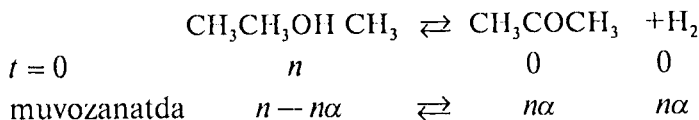


200°C harorat va $9,7 \cdot 10^4 \text{ N/m}^2$ bosimda muvozanat konstantasi $K_p = 6,92 \cdot 10^4 \text{ N/m}^2$ ga teng. 200°C izopropil spirtning dissotsilani sh konstantasi α ni aniqlang. Gaz aralashmasini ideal gazlar qonuniga bo'ysunadi, deb faraz qiling.

Yechish. (V.4) tenglamaga muvofiq:

$$K_p = \frac{P_{\text{as}} \cdot P_{\text{H}_2}}{P_{\text{spirt}}} .$$

Muvozanat konstantasi ifodasini α orqali ifodalash kerak. Agar izopropil spirtning dastlab olingan miqdori n mol bo'lsa, muvozanat qaror topganda moddalarning mol soni quyidagicha ifodalanadi:



$$\sum n_i = (n - n\alpha) + n\alpha + n\alpha = n(1 + \alpha).$$

Demak, Dalton qonuniga muvofiq i - moddaning parsial bosimi P_i :

$$P_i = \frac{n_i}{\sum n_i} P.$$

P — umumiy bosim:

$$P_{\text{spirit}} = \frac{n(1-\alpha)}{n(1+\alpha)} P = \frac{1-\alpha}{1+\alpha} P.$$

$$P_{\text{as}} = P_{\text{H}_2} = \frac{n\alpha}{n(1+\alpha)} P = \frac{\alpha}{1+\alpha} P.$$

Agar bu qiymatlar K_p tenglamasiga qo'yilsa,

$$K_p = \frac{P_{\text{aset.}} \cdot P_{\text{H}_2}}{P_{\text{spirit}}} = \frac{\alpha^2 P}{1-\alpha^2}$$

va bu tenglamadan

$$\alpha^2 = \frac{1}{1 + \frac{P}{K_p}} = \frac{1}{1 + \frac{9,7 \cdot 10^4}{6,92 \cdot 10^4}} = 0,415; \quad \alpha = 0,645.$$

3. $\text{H}_2 + \text{J}_2 \rightleftharpoons 2\text{HJ}$ reaksiyasining 693 K da $K_p = 50,25$ ga teng. Reaksiya uchun $0,846 \cdot 10^{-3}$ kg J_2 va $0,0212 \cdot 10^{-3}$ kg H_2 olib, hajmi 10^{-3} m³ bo'lgan idishga joylashtirilgan. Hosil bo'lgan HJ ning miqdorini aniqlang.

Yechish. (IV.1) tenglamaga muvofiq:

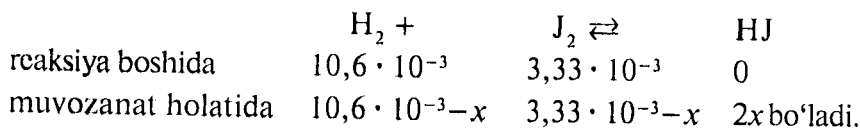
$$K_c = \frac{C_{HJ}^2}{C_{H_2} \cdot C_{J_2}}.$$

Demak, avval dastlab olingan moddalarning konsentratsiyasini, so'ngra muvozanat konsentratsiyalarini aniqlash kerak. $n = \frac{g}{M}$ bo'lganligidan:

$$n_{H_2} = \frac{g_{H_2}}{M_{H_2}} = \frac{0,0212 \cdot 10^{-3} \cdot 10^3}{2} = 0,0106 \text{ mol } H_2.$$

$$n_{J_2} = \frac{g_{J_2}}{M_{J_2}} = \frac{0,846 \cdot 10^{-3}}{254} \cdot 10^3 = 0,00333 \text{ mol } J_2.$$

«kg» dan «g» ga o'tish uchun 10^3 ga ko'paytiriladi. Agar hosil bo'lgan HJ ning miqdorini x deb, 1 mol H_2 va J_2 dan 2 mol HJ hosil bo'lishi e'tiborga olinsa:



Bu qiymatlar yuqoridagi (IV.1) tenglamaga qo'yilsa:

$$K_c = \frac{C_{HJ}^2}{C_{H_2} \cdot C_{J_2}} = \frac{(n_{HJ}/V)^2}{(n_{H_2}/V)(n_{J_2}/V)} = \frac{(4x^2/10^{-3})^2}{\left[\frac{(10,6 \cdot 10^{-3} - x)(3,33 \cdot 10^{-3} - x)}{10^{-3}} \right]} = 50,25.$$

Agar bu tenglama yechilsa:

$$46,26 x^2 - 0,7015 x + 1,4737 \cdot 10^{-3} = 0$$

va

$$x = \frac{0,7015 + \sqrt{0,7025^2 - 4 \cdot 1,7730 \cdot 10^{-3} \cdot 46,25}}{2 \cdot 46,25} = \frac{0,7015 \pm 0,4049}{92,50} \text{ bo'ladi.}$$

Bundan $x_1 = 11,961$; $x_2 = 3,206 \cdot 10^{-3}$ ga teng ekanligini ko'rish mumkin. Hosil bo'lgan HJ miqdori (n_{HJ}) dastlab olingan H_2 va J_2 (n_{H_2} , n_{J_2}) miqdoridan katta bo'lishi mumkin emas. Shunga ko'ra, x_1 bo'lishi mumkin emas. Demak, HJ miqdorida $x_2 = 3,206 \cdot 10^{-3}$ mol. Muvozanat holatda HJ ning gramm miqdori:

$$g_{HJ} = 2xM = 2 \cdot 3,206 \cdot 10^{-3}.$$

4. $N_2O_4 \rightleftharpoons 2NO_2$ reaksiyada $63^\circ C$ da $K_p = 1,27$ ga teng. Umumiy bosim a) 1 atm va b) 10 atm bo'lganda muvozanat holatdagi tarkibini aniqlang.

Yechish, (IV,5) tenglamaga muvofiq:

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

parcial bosimlar aniqlanadi. Bosim 1 atm bo'lganda:

$$P_{N_2O_4} + P_{NO_2} = 1$$

va

$$P_{N_2O_4} = 1 - P_{NO_2}.$$

Demak,

$$K_p = \frac{P_{NO_2}}{1 - P_{NO_2}} = 1,27.$$

Bundan,

$$K_p - K_p P_{NO_2} = P_{NO_2}^2.$$

Bu tenglamaga $K_p = 1,27$ qiymatini qo'yib, P_{NO_2} ga nisbatan yechilsa:

$$P_{\text{NO}_2} = 0,6586 \text{ atm}.$$

$$P_{\text{N}_2\text{O}_4} = 1 - 0,658 = 0,342 \text{ atm}.$$

Daltonning parsial bosimlar qonuniga muvofiq:

$$\frac{n_i}{\sum n_i} = \frac{P_i}{\sum P_i} = N_i.$$

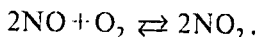
Parsial bosimlar moddalarning molar qismiga proporsional. Tarkibni molar qism foizi bilan ifoda qilish uchun olingan qiymatlarni 100 ga ko'paytirish kerak. Demak, muvozanatdagi aralashma 65,86 % NO_2 va 34,14% N_2O_4 dan iborat.

Xuddi shunday 10 atm uchun:

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}.$$

Bu tenglamaga K_p ning qiymati — 1,27 qo'yilsa va tenglama yuqoridagi kabi yechilsa, $P_{\text{NO}_2} = 2,986 \text{ atm}$, $P_{\text{N}_2\text{O}_4} = 7,02 \text{ atm}$. Demak, aralashmada 29,8 % NO_2 va 70,2 % N_2O_4 bor.

5. 390°C va $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda $0,0157 \text{ NO}_2$ $0,001 - 10^3 \text{ m}^3$ hajmni egallagan. NO_2 quyidagi reaksiya bo'yicha qisman NO va O_2 ga dissotsilanadi:



Reaksiya uchun K_p va K_c ni aniqlang. Gazlar ideal gazlar qonuniga bo'ysunadi, deb faraz qilish mumkin.

Y e c h i s h . (IV.5) tenglamaga muvofiq:

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2 p_{\text{O}_2}}.$$

Bu tenglamadan K_p ni topish uchun barcha moddalarning muvozanat parsial bosimlarini aniqlash kerak. Buning uchun muvozanat holatdagi tarkibini, ya'ni moddalarni qancha mol dan iboratligini bilish kerak bo'ladi. So'ngra Daltonning parsial bosim qonunidan foydalanib, parsial bosimlarni aniqlash mumkin:

$$\frac{n_i}{\sum n_i} = \frac{P_i}{\sum P_i}; \quad P_i = \frac{n_i}{\sum n_i} P; \quad \sum P_i = P \text{ — umumiy bosim.}$$

n_i , $\sum n_i$ larni bilish uchun, o'z navbatida modda qanday darajada dissotsilanganini bilish kerak. Masalan, 1 mol NO_2 to'liq dissotsilanganda reaksiyaga muvofiq 1 mol NO va 0,5 mol O_2 hosil bo'ladi. Agar 1 mol NO_2 ning yarmi dissotsilansa, 0,5 mol NO va 0,25 mol O_2 hosil bo'ladi, dissotsilanmagan NO_2 ning miqdori 1—0,5 mol bo'ladi. Moddaning dissotsilangan qismining umumiy miqdoriga nisbati α — dissotsilanish darajasi deyiladi. Demak, NO_2 ning miqdori n mol, α — dissotsilanish darajasi:

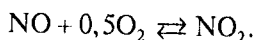
	NO	O_2	NO_2
dissotsilanishdan oldin	0	0	1
dissotsilanishdan so'ng	$n\alpha$	$0,5 n\alpha$	$n - n\alpha = n(1 - \alpha)$

Shunday qilib, dastlabki moddaning mol miqdori va α ma'lum bo'lsa, muvozanatdagi tarkibni aniqlash mumkin. α izotonik koeffitsiyent (i) deb atalgan kattalik orqali aniqlanadi. Agar gaz dissotsilansa, $PV = inRT$ bo'ladi. i — dissotsilanganidan so'ng aralashmadagi mol soni dastlabkisiga nisbatan necha marotaba ko'payganini ko'rsatadi. Agar 1 mol molekula dissotsilanganda n_i mol yangi modda hosil bo'lsa:

$$\alpha = \frac{i-1}{V-1}.$$

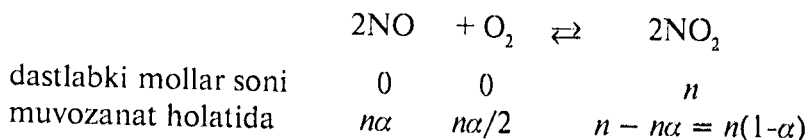
$PV = inRT$, bundan:

$$i = \frac{PV}{nRT} = \frac{1,013 \cdot 10^5 \cdot 0,001}{0,0857 \cdot 8,314 \cdot 663} = 1,17$$



Demak, $V = 1,5$

$$\alpha = \frac{1,17-1}{1,5-1} = 0,34$$



va

$$\sum n_i = n\alpha + \frac{n\alpha}{2} + n(1-\alpha).$$

Yechish. Demak,

$$\frac{n_i}{\sum n_i} = \frac{P_i}{\sum P_i}; \quad P_2 = \frac{n_i}{\sum n_i} \cdot P;$$

$$P_{\text{NO}_2} = \frac{2(1-\alpha)}{\alpha+2} P; \quad P_{\text{O}_2} = \frac{\alpha}{2+\alpha} P; \quad P_{\text{NO}} = \frac{2\alpha}{2+\alpha} P.$$

Agar bu qiymatlar muvozanat konstantasi (K_p) tenglamasiga qo'yilsa:

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \cdot P_{\text{O}_2}} = \frac{(1-\alpha)^2(2+\alpha)}{\alpha^3 P} = \frac{(1-0,34)^2(2+0,34)}{0,34^3 \cdot 1,043 \cdot 10^5} = 25,60 \cdot 10^{-5} (\text{N/m}^2)^{-1}.$$

K_c ni aniqlaymiz:

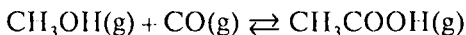
$$K_p = K_c (RT)^{\Delta n}, \quad \Delta n = 2 - (2+1) = -1,$$

$$K_p = K_c RT^{-1} = \frac{K_c}{RT}; \quad K_c = K_p \cdot RT$$

va

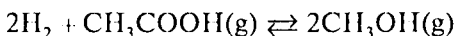
$$K_c = K_p \cdot RT = 25,60 \cdot 10^{-5} \cdot 8,314 \cdot 390 = 1,41 \text{ m}^3/\text{mol}.$$

6. 600 K haroratda



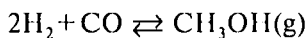
reaksiyada $K_{p,1} = 2,78 \cdot 10^{-9} (\text{N}/\text{m}^2)^{-1}$ ga teng.

600 K da



reaksiyada $K_p = 6,5 \cdot 10^{-6} (\text{N}/\text{m}^2)^{-1}$ ga teng.

600 K da



reaksiyaning muvozanat konstantasi (K_p) ni aniqlang.

Yechish. Reaksiyalarning bosim bo'yicha muvozanat konstantalari muvofiq ravishda teng:

$$\text{a) } K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \cdot P_{\text{CO}}};$$

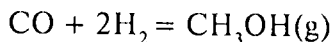
$$\text{b) } K_{p_1} = \frac{P_{\text{CH}_3\text{COOH}}}{P_{\text{CH}_3\text{OH}} \cdot P_{\text{CO}}};$$

$$d) K_{p_2} = \frac{p^2_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \cdot P_{\text{CH}_3\text{COOH}}}.$$

«b» va «d» tenglamalarning o'ng va chap tomonlari o'zaro ko'paytirilsa, «a» tenglama kelib chiqadi.

$$\text{Demak, } K_p = K_{p,1} \cdot K_{p,2} = 2,78 \cdot 10^{-5} \cdot 6,5 \cdot 10^{-6} = 1,8 \cdot 10^{-10} \text{ (N/m}^2\text{)}^{-1}.$$

7. Quyidagi reaksiyada:



523 K va $1,0133 \cdot 10^7$ Pa bosimda konstantasi $K = 2,235 \cdot 10^{-3}$ ga teng, reaksiyada muvozanat qaror topganda CH_3OH ning unumini aniqlang (bosim — atm. birligida berilgan).

Yechish. (IV. 8) — (IV.11) tenglamalardan foydalaniladi:

$$K_A = K_a = \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{CO}} \cdot f_{\text{H}_2}^2} = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \cdot P_{\text{H}_2}^2} \cdot \frac{\gamma_{\text{CH}_3\text{COOH}}}{\gamma_{\text{CO}} \cdot \gamma_{\text{H}_2}^2} = K_p \cdot K_a \cdot P^{\Delta n}.$$

$$K_p = \frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}} \gamma_{\text{H}_2}^2} \text{ qiymatini aniqlashda quyidagi mos holatlar}$$

qiymatlaridan foydalanib, $\gamma = \varphi(\pi, \tau)$ bog'lanish berilgan.

Moddalar	$P \cdot 10^{-5} \text{ Pa}$	π	$T_{\text{krit}} \text{ K}$	τ	γ
CH_3OH	73,54	1,27	513,2	1,02	0,55
CO	34,96	2,90	131,9	3,94	1,05
H_2	12,96	7,82	33,3	15,71	1,06

$$K_y = \frac{0,55}{1,05 \cdot 1,06^2} = 0,466,$$

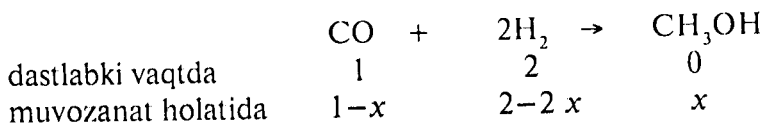
bundan:

$$K_a = 2,235 \cdot 10^{-3} = \frac{x_{\text{CH}_3\text{COOH}}}{x_{\text{CO}} x_{\text{H}_2}^2} \cdot 0,466 \cdot 10^{-1},$$

$$K_c = \frac{x_{\text{CH}_3\text{OH}}}{p_{\text{CO}} p_{\text{H}_2}^2} = \frac{2,235 \cdot 10^{-3}}{0,406 \cdot 0,1} = 47,96.$$

Endi reaksiyadan oldingi va muvozanat holatidagi moddalarning mol miqdorini aniqlaymiz.

Agar x mol CH_3OH hosil bo'lgan bo'lsa:



$$\sum n_i = 1 - x + 2 - 2x + x = 3 - 2x$$

$$x_{\text{CH}_3\text{OH}} = \frac{x}{3-2x} \cdot P; \quad x_{\text{CO}} = \frac{1-x}{3-2x} P; \quad x_{\text{H}_2} = \frac{2-2x}{3-2x} P.$$

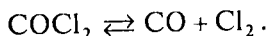
Masala sharti bo'yicha $P = 1$ atm teng bo'lgani uchun:

$$K_c = \frac{x_{\text{CH}_3\text{OH}}}{x_{\text{CO}} \cdot x_{\text{H}_2}^2} = \frac{x(3-2x)^2}{(3-2x)(1-x)^2} = \frac{x(3-2x)^2}{4(1-x)^2} = 47,96.$$

Bu tenglamadan x ni aniqlash uchun x ga nisbatan uchinchi darajali tenglamani yechish kerak. $x = 0,7983$ ga teng. Demak, 1 mol CO va 2 mol H_2 dan:

$0,7983(3-2 \cdot 0,7983) = 0,57$ mol CH_3OH hosil bo'ladi.

8. Fosgen quyidagi reaksiya bo'yicha dissotsilanadi:



600°C va $1,38 \cdot 10^5 \text{ N/m}^2$ bosimda dissotsilanish darajasi $\alpha = 0,9$ ga teng bo'ladi. Komponentlarning quyidagi jadvalda berilgan qiymatlarida reaksiya qaysi tomonga boradi?

N_0	P_{COCl_2}	P_{CO}	P_{Cl_2}
1	$1,013 \cdot 10^5$	$1,013 \cdot 10^5$	$1,013 \cdot 10^5$
2	$1,048 \cdot 10^5$	$2,026 \cdot 10^5$	$3,039 \cdot 10^5$
3	$1,048 \cdot 10^5$	$3,039 \cdot 10^5$	$3,039 \cdot 10^5$

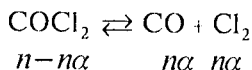
Y e c h i s h . Reaksiya izoterma (IV.17) tenglamasi yordamida izobarik potentsiallarning o'zgarishi aniqlanadi va uning ishorasiga qarab reaksiyaning yo'nalishi belgilanadi:

$$\Delta G = 2,3RT \left(\lg \frac{P_{\text{CO}} \cdot P_{\text{Cl}_2}}{P_{\text{COCl}_2}} - \lg K_p \right).$$

Demak, bu tenglamani yechish uchun, avvalo, K_p aniqlanishi kerak. Buning uchun moddalarning parsial bosimini aniqlash kerak, ya'ni Daltonning parsial bosimlar qonuniga muvofiq:

$$\frac{n_i}{\sum n_i} = \frac{P_i}{\sum P_i}; \quad P_i = \frac{n_i}{\sum n_i} \sum P_i = \frac{n_i}{\sum n_i} P.$$

Demak, parsial bosimlarni aniqlash uchun moddalarning mol soni va ularning yig'indisini topish kerak. Agar COCl_2 dan n mol olingan bo'lsa:



Demak: $\sum n_i = n - n\alpha + n\alpha + n\alpha = n + n\alpha = n(1 + \alpha).$

Muvozanat holatida parsial bosimlar:

$$P_{\text{COCl}_2} = \frac{n(1-\alpha)}{n(1+\alpha)} P = \frac{1-\alpha}{1+\alpha} P;$$

$$P_{\text{CO}} = P_{\text{Cl}_2} = \frac{n\alpha}{n(1+\alpha)} P = \frac{\alpha}{1+\alpha} P.$$

Bu qiymatlar K_p tenglamasi bo'yicha:

1-holatda:

$$K_p = \frac{P_{\text{CO}} \cdot P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{\alpha^2 P}{1-\alpha^2} = \frac{0,9^2 \cdot 1,38 \cdot 10^5}{1-0,9^2} = 5,883 \cdot 10^5 \text{ N/m}^2$$

va

$$\Delta G = 2,3RT \left[\lg \frac{P_{\text{Cl}} \cdot P_{\text{Cl}_2}}{P_{\text{COCl}_2}} - \lg K_p \right] = 2,3 \cdot 8,314 \cdot 873 \times$$

$$\times \left[\lg \frac{1,013 \cdot 10^5 \cdot 1,013 \cdot 10^5}{1,013} - \lg 5,883 \cdot 10^5 \right] = -12,76 \text{ kJ.}$$

Demak, 1-holatda reaksiya to'g'ri tomonga (chapdan o'ngga) boradi.

2-holatda:

$$\Delta G = 2,3 \cdot 8,314 \cdot 873 \left[\lg \frac{2,06 \cdot 10^5 \cdot 3,039 \cdot 10^5}{1,048 \cdot 10^5} - \lg 5,883 \cdot 10^5 \right] = 0.$$

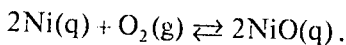
Demak, 2-holatda sistema muvozanat holatida bo'ladi.

3-holatda:

$$\Delta G = 2,3 \cdot 8,314 \cdot 873 \left[\lg \frac{3,039 \cdot 10^5 \cdot 3,039 \cdot 10^5}{1,048 \cdot 10^5} - \lg 5,8834 \right] = 2,93 \text{ kJ.}$$

Bunda reaksiya teskari tomonga borishi mumkin.

9. Quyidagi reaksiyada ΔG ni va U orqali reaksiyaning yo'nalishini aniqlang.



600°C da dissosilanish bosimi $4 \cdot 10^{-17}$ mm simob ustuniga teng. Shu haroratda kislorod $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda olingan.

Yechish. Reaksiya geterogen bo'lganligidan K_p ni hisoblashda qattiq holdagi moddalarning bug' bosimi hisobga olinmaydi:

$$K_p = \frac{1}{P_{\text{O}_2}}$$

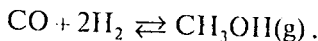
$$\text{va } P_{\text{O}_2} = 4 \cdot 10^{-17} \text{ mm simob ustuni yoki } P_{\text{O}_2} = \frac{4 \cdot 10^{-17} \cdot 1,013 \cdot 10^5}{760} = 5,3310^{-15} \text{ N/m}^2.$$

$$K_p = \frac{1}{5,33 \cdot 10^{-15}} \cdot [\text{N/m}^2]$$

$$\text{va } \Delta G = 2,3 \cdot 8,314 \cdot 873 \left[\lg \frac{1}{1,013 \cdot 10^5} - \lg \frac{1}{5,33 \cdot 10^{-15}} \right] = -321,8 \text{ kJ}.$$

Demak, reaksiya o'ng tomonga boradi.

10. 800 K da metil spirt hosil bo'ladi:



Reaksiyaning K_p ni aniqlang. Quyidagi ma'lumotlardan foydalaning:

$$K_{p,298} = 4,13 \cdot 10^{-10} \text{ N/m}^2; \quad \Delta H_{298}^0 = -90,44 \text{ J/mol} \cdot \text{grad}.$$

Molar issiqlik sig'im C_p lari:

$$C_{p,CO} = 28,41 + 4,1 \cdot 10^{-3} T - 0,46 \cdot 10^{-5} \text{ J/mol} \cdot \text{grad}.$$

$$C_{p,H_2} = 27,28 + 3,26 \cdot 10^{-3} T + 0,562 \cdot 10^{-3} \text{ J/mol} \cdot \text{grad}.$$

$$C_{p,CH_3OH} = 15,28 + 105,2 \cdot 10^{-3} T - 31,04 \cdot 10^{-6} \text{ J/mol} \cdot \text{grad}.$$

Yechish. (IV.20) tenglamaga muvofiq:

$$\lg K_{p,800} = \lg K_{p,298} + \frac{\Delta H_{800}}{2,3R} \left(\frac{800 - 298}{800 \cdot 298} \right).$$

Demak, avval ΔH ning qiymatini aniqlash kerak:

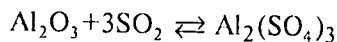
$$\Delta H_{800} = \Delta H_{298}^0 + \int_{298}^{800} \Delta C_p dT$$

$$\Delta C_p = C_{p,CH_3OH} - (C_{p,CO} + 2C_{p,H_2}) = -67,69 + 94,58 \cdot 10^{-3} T - 0,544 \cdot 10^{-5} T^2 - 31,04 \cdot 10^{-6} T^2,$$

$$\begin{aligned} \Delta H_{800} &= -90,44 + \int_{298}^{800} (-67,49 + 94,58 \cdot 10^{-3} T - 0,544 \cdot 10^{-5} T^2 - \\ &- 31,04 \cdot 10^{-6} T^2 dT) = -90,440 - 67,49(800 - 298) + \frac{94,58 \cdot 10^{-3}}{2} \times \\ &\times (800^2 - 298^2) + 0,54 \cdot 10^5 \left(\frac{1}{800} - \frac{1}{298} \right) - \frac{31,04 \cdot 10^6}{3} (800^3 - 298^3) = \\ &= 103700 \text{ J} = 103,7 \text{ kJ}, \end{aligned}$$

$$\lg K_{p800} = \lg 4,13 \cdot 10^{-10} - \frac{103,7 \cdot 10^3}{2,3 \cdot 8,314} \cdot \frac{800-298}{800 \cdot 298} = 1,5 \cdot 10^{-21}.$$

11. 298 K da quyidagi reaksiyaning



muvozanat konstantasi K_p ni aniqlang. Moddalarning standart hosil bo'lish issiqlik effekti ΔH_{298}^0 va standart entropiya S_{298}^0 qiymati berilgan:

ΔH_{298}^0 , kJ/mol	$\text{Al}_2(\text{SO}_4)_3$	Al_2O_3	SO_2
	- 3434	- 1675	- 395,2
S_{298}^0 , J/mol · grad.	239,2	50,94	256,23

Yechish. (IV.24) va (III.10) tenglamalardan foydalaniladi:

$$\lg K_{p,298} = -\frac{\Delta G_{298}^0}{2,3RT}.$$

O'z navbatida, (III.10) tenglamaga muvofiq:

$$\begin{aligned}\Delta G_{298}^0 &= \Delta H_{298}^0 - T\Delta S_{298}^0 \\ \Delta H_{298}^0 &= \Delta H_{298, \text{Al}_2(\text{SO}_4)_3}^0 - \left(\Delta H_{298, \text{Al}_2\text{O}_3}^0 + \Delta H_{298, \text{SO}_2}^0 \right) = \\ &= -3434 - (-1675 - 3 \cdot 395,2) = -573,4 \text{ kJ}, \\ \Delta S_{298}^0 &= S_{298, \text{Al}_2(\text{SO}_4)_3}^0 - \left(S_{298, \text{Al}_2\text{O}_3}^0 + S_{298, \text{SO}_2}^0 \right) = \\ &= 239,2 - (50,92 + 3 \cdot 256,23) = -580,43 \text{ J/mol} \cdot \text{grad}\end{aligned}$$

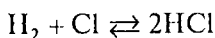
va

$$\Delta G_{298}^0 = -573,4 \cdot 10^3 - 298(-580,43) = -400,43 \cdot 10^3 \text{ J}.$$

$$\lg K_{p,298} = -\frac{\Delta G_{298}^0}{2,3RT} = -\frac{400,42 \cdot 10^3}{2,3 \cdot 8,314 \cdot 298} = -70,26.$$

$$K_p = 2,74 \cdot 10^{-71}.$$

12. Xlorid kislota HCl ning hosil bo'lish reaksiyasi:



muvozanat konstantasi harorati bilan quyidagicha bog'langan:

$$\lg K_p = \frac{9411,7}{T} - 1,312 \lg T + 0,128 \cdot 10^{-3} T + \frac{0,11 \cdot 10^5}{T^2} + 4,9.$$

1000 K da reaksiyaning issiqlik effektini aniqlang.

Yechish. (IV.21) tenglamadan:

$$\Delta H = \frac{RT^2 d \ln K_p}{dT}.$$

Demak, $\lg K_p$ ni $\ln K_p$ ga aylantirib, T ni differensiyalash kerak. Buning uchun tenglamaning o'ng tomonini 2,303 ga ko'paytirish kerak:

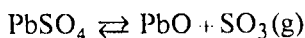
$$\ln K_p = \frac{21,675 \cdot 10^{-3}}{T} - 2,99 \ln T + 0,295 \cdot 10^{-3} T + \frac{0,253 \cdot 10^5}{T^2} + 11,28,$$

$$\Delta H_T^0 = RT^2 \left(-\frac{21,675 \cdot 10^{-3}}{T^2} - \frac{2,99}{T} + 0,295 \cdot 10^{-3} - \frac{0,506 \cdot 10^5}{T^3} \right) =$$

$$= -180,19 \cdot 10^3 - 10,918T + 2,45 \cdot 10^{-3} T^2 - \frac{4,207 \cdot 10^5}{T},$$

$$\begin{aligned} \Delta H_{1000} &= -180,19 \cdot 10^3 - 10,918 \cdot 10^3 + 2,45 \cdot 10^3 - \\ &- 0,42 \cdot 10^3 = -189,07 \cdot 10^3 \text{ J.} \end{aligned}$$

13. Quyidagi reaksiya



uchun berilgan ma'lumotlardan foydalanib, 400 K da muvozanat konstanta (K_p)ni aniqlang. Quyida ΔH_{298}^0 — moddalarning standart hosil bo'lish issiqlik effektlari, S_{298}^0 — standart entropiyalari, C_p — moddalarning bosim o'zgarmas bo'lgandagi issiqlik sig'implarining haroratga bog'liqlik tenglamalari keltirilgan.

$$\Delta H_{298}^0 (\text{RbSO}_4) = -219500 \text{ kal/mol},$$

$$\Delta H_{298}^0 \text{ RbO} = -52070 \text{ kal/mol},$$

$$\Delta H_{298}^0 (\text{SO}_3) = -94400 \text{ kal/mol},$$

$$S_{298}^0 (\text{RbSO}_4) = 35,2 \text{ kal/mol} \cdot \text{grad},$$

$$S_{298}^0 (\text{RbO}) = 16,6 \text{ kal/mol} \cdot \text{grad},$$

$$S_{298}^0 (\text{SO}_3) = 61,24 \text{ kal/mol} \cdot \text{grad}.$$

$$C_p(\text{RbSO}_4) = 10,96 + 31 \cdot 10^{-3} T + 4,2 \cdot 10^5 T^{-2},$$

$$C_p(\text{RbO}) = 10,60 + 4 \cdot 10^{-3} T,$$

$$C_p(\text{SO}_3) = 13,7 + 6,42 \cdot 10^{-3} T + 3,12 \cdot 10^5 T^{-2}.$$

Y e c h i s h . (IV.24) tenglamaga muvofiq:

$$\lg K_p = -\frac{\Delta G}{2,3RT}.$$

Shuningdek, ΔG ning qiymati (IV.25) tenglamadan foydalanib aniqlanadi: $\Delta G_T = \Delta H_T - T\Delta S_T$.

Bundan:

$$\begin{aligned} \Delta H_{298}^0 &= \left(\Delta H_{298, \text{PbO}}^0 + \Delta H_{298, \text{SO}_3}^0 \right) - \left(\Delta H_{298, \text{PbSO}_4}^0 \right) = \\ &= (-52070 - 94400 - (-219500)) = 72980 \text{ kal}. \end{aligned}$$

$$\begin{aligned} \Delta S_{298}^0 &= \left(S_{298, \text{PbO}}^0 + S_{298, \text{SO}_3}^0 \right) - \left(S_{298, \text{PbSO}_4}^0 \right) = \\ &= (16,6 + 61,24) - (35,2) = 42,64 \text{ kal/mol} \cdot \text{grad}. \end{aligned}$$

$$\Delta C_p = \left(C_{p, \text{PbO}} + C_{p, \text{SO}_3} \right) - \left(C_{p, \text{PbSO}_4} \right) = 13,7 + 6,42 \cdot 10^{-3} T + 3,12 \cdot 10^5 T^{-2}.$$

$$\Delta H_{400} = \Delta H_{298}^0 + \int_{298}^{400} \Delta C_p dT;$$

$$\Delta S_{400} = \Delta S_{298}^0 + \int_{298}^{400} \frac{\Delta C_p}{T};$$

va

$$\Delta G_{400} = \Delta H_{298}^0 - T \Delta S_{298}^0 + \int_{298}^{400} \Delta C_p dT + \int_{298}^{400} \frac{\Delta C_p dT}{T};$$

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R} - \int_{298}^{400} \Delta C_p dT + \frac{1}{2,3R} \int_{298}^{400} \frac{\Delta C_p}{T} dT.$$

1-taxmin. Agar $\Delta C_p = 0$ deb faraz qilinsa, (IV.26) tenglamaga muvofiq:

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R} = -\frac{72980}{4,57 \cdot 400} + \frac{42,64}{4,57} = -39,92 + 9,33 = -30,59;$$

$$K_p = 3 \cdot 10^{-31} (R = 1,98 \text{ kal/mol} \cdot \text{grad}).$$

2-taxmin. Agar $C_p \neq f(T)$, ya'ni C_p haroratga bog'liq emas — turg'un deb faraz qilinsa, (IV.29) tenglamaga muvofiq:

$$\lg K_p = -\frac{\Delta H_{298}^0}{2,3RT} + \frac{\Delta S_{298}^0}{2,3R} - \frac{\Delta C_p}{2,3RT} \left[(T - 298) - T \lg \frac{T}{298} \right].$$

Ma'lumotnomalardan olingan ma'lumotlarga muvofiq o'rtacha C_p :

$$C_{p(\text{PbSO}_4)} = 26,15 \text{ kal/grad}; \quad C_{p(\text{RbO})} = 15,81;$$

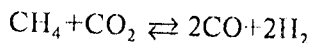
$$C_{p,\text{SO}_3} = 14,17 \text{ kal/grad}; \quad \Delta C_p = 14,17 + 15,81 - 26,15 = 3,83;$$

$$\begin{aligned} \lg K_p &= -39,92 + 9,33 - \frac{3,83}{4,57 \cdot 400} (400 - 298) - 400 \lg \frac{400}{298} = \\ &= -30,59 + 0,17 = -30,76. \end{aligned}$$

Agar tenglamani Temkin-Shvarsman bo'yicha yechsak, ma'lumotnomadan olingan ($M_0 = 0,0392$; $M_1 = 0,0130 \cdot 10^3$ va $M_2 = 0,0364 \cdot 10^5$) qiymatlar (IV.31) tenglamaga qo'yiladi:

$$\lg K_p = -\frac{56,54}{4,57 \cdot 400} = -30,39, \quad K_p = 4,0710^{-31}.$$

14. Temkin-Shvarsman usuli bilan 1200 K da quyidagi reaksiya uchun:



muvozanat konstantasi K_p ni aniqlang.

Kerakli ma'lumotlar quyidagi jadvalda berilgan:

Modda	ΔH_{298}^0 , kJ/mol	ΔS_{298}^0 , J/mol $\times$ grad	$C_p = f(T)$				
			a	$b \cdot 10^3$	$c \cdot 10^6$	$e_1 \cdot 10^{-5}$	$d \cdot 10^9$
CO	-110,5	197,4	28,41	4,10	—	0,46	—
H ₂	0	130,6	27,28	3,26	—	0,502	—
CH ₄	-74,85	186,2	17,45	60,46	1,117	—	-7,20
CO ₂	-393,5	213,6	44,14	9,04	—	-8,63	—

Yechish. Bu ma'lumotlardan ΔH_{298}^0 , ΔS_{298}^0 , Δa , Δb , Δc , $\Delta c'$, Δd larning qiymati hisoblanadi:

$$\Delta H_{298}^0 = \left[2\Delta H_{298}^0(\text{CO}) + 2\Delta H_{298}^0(\text{H}_2) \right] - \left[\Delta H_{298}^0(\text{CH}_4) + \Delta H_{298}^0(\text{CO}_2) \right] = 247,35 \text{ kJ/mol};$$

$$\Delta S_{298}^0 = \left[\left(2S_{298}^0(\text{CO}) + 2\Delta H_{298}^0(\text{H}_2) \right) \right] - \left[\left(\Delta S_{298}^0(\text{CH}_4) + \Delta S_{298}^0(\text{CO}_2) \right) \right] = 256,2 \text{ J/mol} \cdot \text{grad};$$

$$\Delta a = [2a_{(\text{CO})} + 2a_{(\text{H}_2)}] - [a_{\text{CH}_4} + a_{\text{CO}_2}] = 49,78 \text{ J/mol} \cdot \text{grad};$$

$$\Delta b = [2b_{(\text{CO})} + 2b_{(\text{H}_2)}] - [b_{\text{CH}_4} + b_{\text{CO}_2}] = -54,78 \cdot 10^{-3} \text{ J/mol} \cdot \text{grad};$$

$$\Delta c = -c_{\text{CH}_4} = -1,117 \cdot 10^{-6} \text{ J/mol} \cdot \text{grad};$$

$$\Delta c^1 = -2c_{\text{CO}}^1 + 2c_{\text{H}_2}^1 - c_{\text{CO}_2}^1 = 8,614 \cdot 10^5 \text{ J/mol} \cdot \text{grad};$$

$$\Delta d = -d_{\text{CH}_4} = -7,20 \cdot 10^{-9} \text{ J/mol} \cdot \text{grad}.$$

Ma'lumotnomadan quyidagi qiymatlarni olib,

$M_0 = 0,641$, $M_1 = 0,339$, $M_2 = 0,203$, $M_{-2} = 0,318$,
 $M_3 = 0,137$ (IV.30, IV.31) tenglamalarga qo'yilsa:

$$\begin{aligned} \lg K_p &= -\frac{247350}{2,3 \cdot 8,314 \cdot 1200} + \frac{256,2}{2,3 \cdot 8,314} + \frac{1}{2,3 \cdot 8,314} = \\ &= (31,93 - 18,57 - 0,227 + 2,739 + 0,986) = 3,5006 \end{aligned}$$

va

$$K_p = 3,166 \cdot 10^3.$$

15. 800 K da quyidagi reaksiya uchun muvozanat konstantasi K_p ni aniqlang.



Masalani yechishda quyidagi $\frac{\Delta G^0 - H_0^0}{T}$ va ΔH_0^0 qiymatlardan foydalaning.

	C_4H_6	H_2	C_4H_{10}
ΔH_0^0 , kJ/mol	125,95	0	-97,981
$\frac{G^0 - H_0^0}{T}$ J/mol · grad.	-298,07	-130,482	-333,17

Yechish. (IV.33) tenglamaga muvofiq Δ hisoblab chiqiladi:

$$\Delta \left(\frac{G_{800} - H_0^0}{T} \right) = [(-298,07) + (-2 \cdot 130,482)] -$$

$$- [-333,17] = -225,864 \text{ J/grad.}$$

$$\Delta H^0 = 125,95 - (-97,981) = 223,931 \text{ kJ.}$$

$$\lg K_p = \frac{1}{2,3R} \left[\Delta \left(\frac{G_{800} - H}{T} + \frac{\Delta H_0}{T} \right) \right] =$$

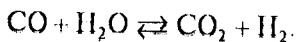
$$= \frac{1}{2,3 \cdot 8,314} \left[-225,864 + \frac{223,931}{800} \right] = -2,8233$$

$$\lg K = -2,8233; \quad K_p = 0,0015.$$

MASALALAR

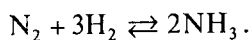
1. $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ reaksiyaning muvozanat holatida CO_2 , H_2 , CO , H_2O larning parsial bosimlari mos ravishda 0,116, 0,484, 0,200 va 0,200 atm ga teng: a) reaksiyaning muvozanat konstantasi K_p ni aniqlang; b) muvozanat holatdagi 15 mol CO , 15 mol H_2O va 65,16 mol CO_2 bilan muvozanatda bo'lgan vodorod necha mol?

2. 1 mol CO , 1 mol H_2O , 1 mol H_2 va 1 mol CO_2 dan iborat gaz aralashmasida quyidagi reaksiya borgan:



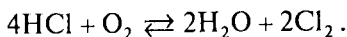
Muvozanat holatda CO ning miqdori 0,16 mol ga teng. Reaksiyaning muvozanat konstantasi K_p ni aniqlang.

3. 1 mol azot va 3 mol vodorod aralashmasi bilan quyidagi reaksiya o'tkazilgan:



10,13 10^5 N/m^2 bosimda (muvozanat holatida) 0,5 mol NH_3 hosil bo'lgan. K_p ni aniqlang. Hajm hisobida NH_3 aralashmaning necha foizini tashkil qiladi?

4. 4,9 mol HCl va 5,1 mol O_2 olib, 480°C da quyidagi reaksiya o'tkazilgan:

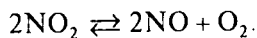


Muvozanat holatida bosim 723 mm simob ustuniga teng. Olingan HCl ning 76%i reaksiyaga kirishgan. Reaksiyaning muvozanat konstantasi K_p ni aniqlang.

5. $0,5\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$ reaksiyaning K_p va K_c sini aniqlang.

N_2O_4 ning dissotsilanish darajasi $\alpha = 0,533$, bosim $5,40 \cdot 10^4 \text{ Pa}$.

6. 767 K va $9,899 \cdot 10^4 \text{ Pa}$ bosimda azot (IV) oksid NO_2 quyidagi reaksiya bo'yicha dissotsilangan:



a) reaksiyaning K_p va K_c si aniqlangan;

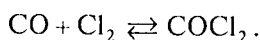
b) shu haroratda NO_2 ning 80% i dissotsilanishi uchun bosim qanchaga teng bo'lishi kerak?

7. PCl_5 quyidagicha dissotsilanadi:



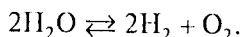
500 K va 1 atm bosimda muvozanatdagi 1 litr aralashmadagi 3,133 g α va K_p ni aniqlang.

8. 1 mol CO va 1 mol Cl_2 gazlaridan iborat aralashma 550°C va 1 atm da reaksiyaga kirishgan:



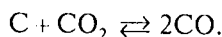
Muvozanat holatda 0,2 mol COCl_2 hosil bo'lgan. K_p va K_c ni aniqlang.

9. 2500 K da va 1 atm bosimda suv bug'i 4,20% dissotsilangan:



K_p ni aniqlang.

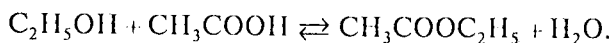
10. Uglerod CO_2 bilan quyidagicha reaksiyaga kirishadi:



Muvozanat holatda 900 K va 1 atm da gaz aralashmasining mol hisobida 35,28% ini CO tashkil qilgan. K_p ni aniqlang va 10 atm bosimda muvozanatda qancha CO hosil bo'ladi?

11. 30°C da quyidagi reaksiyaning $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ muvozanat konstantasi $K_c = 2,9 \cdot 10^{-2}$ ga teng. 30°C va 0,5 atm da SO_2Cl_2 ning dissotsilanish konstantasini aniqlang.

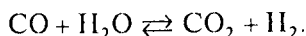
12. Quyidagi efilanish reaksiyasida $K_p = 3,3$ ga teng.



Agar reaksiya uchun 1 mol spirt va 1 mol kislota olinsa, qancha efir hosil bo'ladi?

13. 500 K da quyidagi reaksiyaning $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$ muvozanat konstantasi $K_p = 2,961 \cdot 10^{-5} (\text{N/m}^2)^{-1}$ ga teng. Umumiy bosim $8,201 \cdot 10^5 \text{ N/m}^2$ bo'lganda 500 K da dissotsilanish (α) darajasi qanchaga teng bo'ladi?

14. 20% CO va 80% H_2O aralashmasi 800 K gacha isitilgan:



$K_p = 4,12$ ga teng. Muvozanat holatdagi aralashma tarkibini va 1 kg suv bug'i olinganda qancha vodorod hosil bo'lishini aniqlang.

15. 375 K da $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ reaksiyaning muvozanat konstantasi $K_c = 9,27$ ga teng. SO_2 va Cl_2 dan 1 kmol/ m^3 dan olinsa, SO_2Cl_2 ning muvozanat holatidagi konsentratsiyasini aniqlang.

16. 445 K da quyidagi reaksiyaning $\text{H}_2 + \text{J}_2 \rightleftharpoons 2\text{HJ}$ muvozanat konstantasi $K_p = 50$ ga teng. 1,27 g yod va 0,02 g vodorod 445 K gacha isitilganda muvozanat holatdagi aralashma hajmi 1 l ga teng bo'lgan. Necha mol HJ hosil bo'ladi va gaz aralashmalarining muvozanat parsial bosimlarini aniqlang.

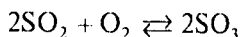
17. 1400 K da reaksiya $\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$ da $K_p = 0,78$ ga teng. Umumiy bosim 1 atm bo'lganda muvozanatda gaz aralashmasining tarkibini aniqlang.

18. Quyidagi reaksiya $2\text{CuCl} + \text{H}_2 \rightleftharpoons 2\text{Cu} + 2\text{HCl}$ da $K_p = 2,1$ ga teng. Reaksiya boshlanishidan avval gaz fazada 0,1 mol H_2 va 0,02 mol HCl bo'lsa, muvozanat holatda umumiy bosim 1 atm ga (parsial bosim atmosfera bilan ifodalansa) teng bo'lgan. Necha gramm Cu hosil bo'lganligini aniqlang.

19. 400°C va $10,13 \cdot 10^5 \text{ N/m}^2$ da ammiakning dissotsilanish darajasi (α) va muvozanat aralashmasidagi ammiakning foiz miqdorini aniqlang.

400°C da reaksiyaning muvozanat konstantasi $K_p = 78,59 \cdot 10^5$ N/m²ga teng.

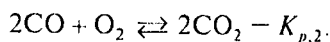
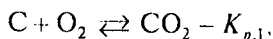
20. 727 K da quyidagi reaksiyada



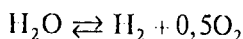
$K_p = 3,417 \cdot 10^5$ (N/m²)⁻¹ ga teng. Qanday bosim ostida SO₃ 20% gacha dissotsilanadi?

SO₃ ning dissotsilanishini 5% gacha kamaytirish uchun bosim qancha bo'lishi kerak?

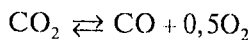
21. $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ reaksiyaning muvozanat konstantasi K_p ni quyidagi reaksiyalar muvozanat konstantalari orqali aniqlang:



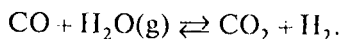
22. 1500 K da suv bug'ining quyidagi reaksiya bo'yicha



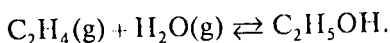
dissotsilanish darajasi $\alpha = 2,21 \cdot 10^{-4}$ ga teng. CO₂ ning shu haroratda quyidagi reaksiya bo'yicha



dissotsilanish darajasi $\alpha = 4,8 \cdot 10^{-4}$ ga teng. Shu haroratda quyidagi reaksiyaning muvozanat konstantasi K_p ni aniqlang:

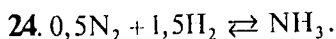


23. 300°C va 10133,0 N/m² bosimda stexiometrik miqdorda C₂H₄ va H₂O reaksiyaga kirishgan:



Reaksiyaning muvozanat konstantasi $K_f = 4,566 \text{ (kN/m}^2\text{)}^{-1}$ ga teng. Etil spirtining unumini aniqlang (reaksiya unumi deb mahsulot mol sonining muvozanat aralashmasidagi umumiy mollar soniga nisbatining hajmda ifodalangan foiziga aytiladi).

$$\gamma_{\text{C}_2\text{H}_4} = 0,958; \quad \gamma_{\text{H}_2\text{O}} = 0,78; \quad \gamma_{\text{C}_2\text{H}_5\text{OH}} = 0,642.$$

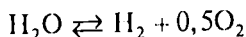


Mazkur jarayonda stexiometrik miqdorda N₂ va H₂ 700 K va 405,3 · 10⁵ N/m² bosimda reaksiyaga kiritilgan. Reaksiyada ΔG ning o'zgarishi quyidagicha:

$$\Delta G = -37949 + 72,757 \lg T - 16,61 \cdot 10^{-3} T^2 + 1,40 \cdot 10^{-6} T^{-3}.$$

Ammiakning unumini aniqlang.

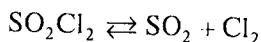
25. 1500°C va 1,013 · 10⁵ N/m² bosimda quyidagi reaksiyada



dastlabki moddalarning parsial bosimlari jadvalda keltirilgan miqdorda bo'lsa, reaksiya qaysi tomonga boradi?

$P_{\text{H}_2\text{O}}, \text{N/m}^2$	$P_{\text{H}_2}, \text{N/m}^2$	$P_{\text{O}_2}, \text{N/m}^2$
$1,013 \cdot 10^5$	$1,013 \cdot 10^3$	$1,013 \cdot 10^5$
$1,013 \cdot 10^4$	$2,026 \cdot 10^2$	$1,25 \cdot 10^{-3}$
$1,013 \cdot 10^4$	$1,013 \cdot 10^1$	$1,26 \cdot 10^{-3}$

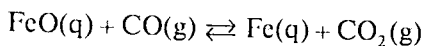
26. Quyidagi reaksiya



30°C da olib borilganda, $K_p = 2,88 \cdot 10^3 \text{ N/m}^2$ ga teng bo'lgan. Dastlabki moddalarning parsial bosimlari quyida jadvalda keltirilgan miqdorda bo'lsa, reaksiya qaysi tomonga boradi?

$P_{\text{SO}_2\text{Cl}_2}, \text{N/m}^2$	$P_{\text{SO}_2}, \text{N/m}^2$	$P_{\text{Cl}_2}, \text{N/m}^2$	T, K
$4,052 \cdot 10^5$	$2,026 \cdot 10^5$	$2,026 \cdot 10^5$	
$3,565 \cdot 10^3$	$1,013 \cdot 10^3$	$1,013 \cdot 10^4$	
$2,026 \cdot 10^3$	$1,013 \cdot 10^3$	$1,013 \cdot 10^4$	700

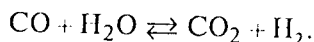
27. Quyidagi reaksiya



1000 K va $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda olib borilganda, CO_2 ning parsial bosimi 265 mm simob ustuniga teng bo'lganda muvozanat qaror topadi. Reaksiyaga olingan moddalarning dastlabki parsial bosimlari quyidagi jadvalda keltirilgan miqdorda bo'lganida reaksiya qaysi tomonga boradi?

$P_{\text{CO}}, \text{N/m}^2$	$P_{\text{CO}_2}, \text{N/m}^2$
$2,026 \cdot 10^5$	$4,02 \cdot 10^5$
$1,62 \cdot 10^5$	$3,039 \cdot 10^5$
$2,026 \cdot 10^5$	$2,026 \cdot 10^5$

28. 930 K da quyidagi reaksiyada $K_p = 1$ ga teng:

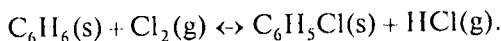


Agar shu haroratda gaz aralashmasi $\text{CO} = 50$, $\text{CO}_2 = 20$, $\text{H}_2 = 25$, $\text{H}_2\text{O} = 5$ tarkibda (hajmiy % hisobida) bo'lsa, reaksiya qaysi tomonga boradi?

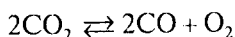
29. 300°C va $1,013 \cdot 10^5 \text{ N/m}^2$ da quyidagi $2\text{HJ} \rightleftharpoons \text{H}_2 + \text{J}_2$ reaksiyada HJ ning dissotsilanish darajasi $\alpha = 20\%$ ga teng bo'ladi. Dastlabki moddalarning jadvalda keltirilgan parsial bosimlarida reaksiya qaysi tomonga boradi?

$P_{\text{HJ}}, \text{N/m}^2$	$P_{\text{H}_2}, \text{N/m}^2$	$P_{\text{J}_2}, \text{N/m}^2$
$3,039 \cdot 10^1$	$3,039 \cdot 10^1$	$5,07 \cdot 10^1$
$3,039 \cdot 10^1$	$3,039 \cdot 10^1$	$4,76 \cdot 10^2$
$3,039 \cdot 10^1$	$3,039 \cdot 10^1$	$1,013 \cdot 10^3$

30. Agar 25°C da $\Delta G_{298, \text{C}_6\text{H}_5\text{Cl}}^0 = 198,4 \text{ kJ/mol}$; $\Delta G_{298, \text{HCl}}^0 = -95,28 \text{ kJ/mol}$, $\Delta G_{298, \text{C}_6\text{H}_6}^0 = 124,6 \text{ kJ/mol}$; $\Delta G_{298, \text{Cl}_2}^0 = 66,454 \text{ kJ/mol}$ bo'lsa, quyidagi reaksiya borishi mumkinmi?:



31. Quyidagi reaksiyada 1000 K da $K_p = 10^{-2}$ ga teng.



1000 — 2000 K da reaksiya issiqlik effekti o'rtacha $\Delta H = -134160 \text{ kal}$. Reaksiyaning 2000 K dagi muvozanat konstantasini aniqlang.

32. 1080 K da reaksiyaning muvozanat konstantasi $K_p = 1$ ga teng. Qanday haroratda $K_p = 27,56$ ga teng bo'ladi, reaksiyaning issiqlik effekti $\Delta H = 9848 \text{ kal}$.

33. RSI₅ ning 473 K va $1,0133 \cdot 10^5 \text{ Pa}$ dagi dissotsilanish darajasi $\alpha = 0,485$ va 523 K . Shu bosimda $\alpha = 0,8$ ga teng. $R = \text{const}$ bo'lganida

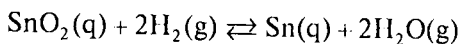
$\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$ reaksiyaning 473 – 523°C chegarasida o‘rtacha issiqlik effektini aniqlang.

34. $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$. Yuqoridagi reaksiyada muvozanat konstantasi harorat bilan quyidagicha bog‘langan:

$$\lg K = \frac{-9876}{T} + 8,18 \lg T - 1,96 \cdot 10^{-2} T - 11,4.$$

Reaksiyaning 1000 K dagi issiqlik effektini aniqlang.

35. Quyidagi reaksiyaning



muvozanat konstantasi harorat bilan quyidagicha bog‘langan:

$$\lg K_p = -\frac{2968}{T} - 1,656 \lg T - 9,08 \cdot 10^{-3} T + 8,416.$$

1073 K da K_p va ΔH ni aniqlang.

36. $2\text{H} \rightarrow \text{H}_2$ reaksiyaning muvozanat konstantasi harorat bilan quyidagicha bog‘langan:

$$\lg K_p = \frac{22570}{T} - 1,504 \lg T - 0,767.$$

800 K da K_p va ΔH ni aniqlang.

37. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ reaksiyaning muvozanat konstantasi harorat bilan quyidagicha bog‘langan:

$$\lg K_c = \frac{24900}{T} - 1,335 \lg T - 9,65 \cdot 10^{-5} T - 1,37 \cdot 10^{-7} T^2 + 1,08.$$

$\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ reaksiya uchun:

$$\lg K_c = \frac{95,86}{T} - 0,44 \lg T + 2,6.$$

$4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ reaksiya uchun 800 K da K_s va ΔH ni aniqlang.

38. a) $\text{C}_6\text{H}_6 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$ va b) $\text{C}_6\text{H}_5\text{CH}_3 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{11}\text{CH}_3$ reaksiyalari muvozanat konstantalari harorat bilan quyidagicha bog'langan:

$$\text{a) } \lg K_{p,a} = \frac{9590}{T} - 9,9194 \lg T + 0,002284T + 8,566;$$

$$\text{b) } \lg K_{p,b} = \frac{10970}{T} - 20,387.$$

$\text{C}_6\text{H}_{11}\text{CH}_3 + \text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_{12}$ reaksiyaning 400°C dagi muvozanat konstantasi K_p va issiqlik effektini (ΔH) aniqlang.

39. a) $2\text{CuCl} \rightleftharpoons 2\text{Cu} + \text{Cl}_2$ va b) $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ reaksiyalarining muvozanat konstantalari harorat bilan quyidagicha bog'langan:

$$\text{a) } \lg K_{p,a} = \frac{13638}{T} + 0,4534 \lg T - 0,109 \cdot 10^{-4} T + 3,426;$$

$$\text{b) } \lg K_{p,b} = \frac{5,272}{T} - 2,01 \lg T - 0,766.$$

$2\text{CuCl(g)} + \text{CO} \rightleftharpoons 2\text{Cu(q)} + \text{COCl}_2$ reaksiyaning muvozanat konstantasi K_p va issiqlik effekti ΔH ning 1000 K dagi qiymatini aniqlang.

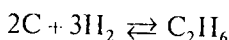
40. $4\text{NO} + 6\text{H}_2\text{O} \rightleftharpoons 4\text{NH}_3 + 5\text{O}_2$ reaksiyaning 1000 K da muvozanat konstantasi K_p va reaksiyaning issiqlik effektini aniqlang. Muvozanat konstantasi harorat bilan quyidagicha bog'langan:

$$\lg K_p = -\frac{47500}{T} - 1,751 \lg T - 8,7.$$

41. Temkin-Shvarsman usulidan foydalanib, gaz fazasida 800 K va $1,0133 \cdot 10^5$ Pa bosimda borayotgan $2C_6H_5CH_3(g) \rightleftharpoons C_6H_4 \times (CH_3)_{2(g)} + C_6H_6(g)$ reaksiyaning ΔG sini aniqlash orqali muvozanat konstantasi qiymatini va muvozanat holatdagi aralashma tarkibini (molar qism ifodasida) aniqlang.

Kerakli ma'lumotlar ilova (ma'lumotnoma)dan olingan.
 $M_0 = 35,97$; $M_1 = 0,1574 \cdot 10^3$; $M_2 = 0,0733 \cdot 10^6$.

42. Quyidagi ma'lumotlardan foydalanib, 298 K da reaksiyaning muvozanat konstantasi (K_p) ni aniqlang:



$$\Delta H_{298, C_6H_6}^0 = -20236 \text{ kal/mol} \cdot \text{grad. } \Delta H_{298, C}^0 = 0; \Delta H_{298, H_2}^0 = 0;$$

$$S_{298, C_2H_6}^0 = 54,85 \text{ kal/mol} \cdot \text{grad. } S_C^0 = 1,361 \text{ kal/mol} \cdot \text{grad.}$$

$$S_{H_2}^0 = 31,21 \text{ kal/mol} \cdot \text{grad.}$$

43. 25°C da $H_2 + Cl_2 \rightleftharpoons 2HCl$ reaksiyaning muvozanat konstantasi K_p ni aniqlang. Shu haroratda reaksiyaning issiqlik effekti $\Delta H_{298}^0 = 44126$ kal. $S_{H_2}^0 = 31,211$ kal/mol · grad. $S_{Cl_2}^0 = 53,286$ kal/mol · grad. $S_{HCl}^0 = 44617$ kal/mol · grad.

44. 1000 K da $CO + H_2O \rightleftharpoons CO_2 + H_2$ reaksiyaning muvozanat konstantasi K_p ni aniqlang. Quyidagi ma'lumotlardan foydalangan holda: $\Delta H_{298, CO_2}^0 = -91052$ kal/mol; $\Delta H_{298, CO}^0 = -26416$ kal/mol; $\Delta H_{298, H_2O}^0 = -57799$ kal/mol; $S_{CO_2}^0 = 51,06$ kal/mol · grad; $S_{H_2}^0 = -31,211$ kal/mol · grad. $S_{CO}^0 = 47,301$ kal/mol · grad; $S_{H_2O}^0 = -45,100$ kal/mol · grad. $\Delta C_p = 1,72$ kal/mol · grad.

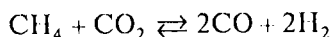
45. Quyidagi ma'lumotlardan foydalanib, $\text{NiS}(\text{q}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{NO}(\text{q}) + \text{H}_2(\text{g})$ reaksiya uchun 600 K dagi K_p ni aniqlang.

№	Modda	kkal/mol × × grad	S, kal/mol × × grad	Issiqlik sig'imi, kal/mol · grad		
				$C = f(T)$ tenglama koeffitsiyentlari		
				a	$b \cdot 10^3$	$c \cdot 10^{-5}$
1	NO	-58,4	9,22	13,69	0,83	-2,91
2	H ₂ S	-4,815	49,15	7,10	3,25	—
3	NiS	-18,6	13,4	9,28	3,40	—
4	H ₂ O _(g)	-57,798	45,166	7,20	2,70	—
5	H ₂ O _(s)	-58,217	26,217	—	—	—

46. 400 K da $\text{PbSO}_4 \rightleftharpoons \text{PbO} + \text{SO}_2(\text{g})$ (2) reaksiyaning K_p ini aniqlang. Quyidagi ma'lumotlardan foydalaning.

$\Delta H_{298, \text{PbSO}_4}^0 = -219500$ kal/mol; $\Delta H_{298, \text{PbO}}^0 = -52070$ kal/mol;
 $\Delta H_{298, \text{SO}_2}^0 = -54450$ kal/mol; $S_{298, \text{PbSO}_4}^0 = -35,2$ kal/mol · grad;
 $S_{\text{PbO}}^0 = 16,6$ kal/mol · grad; $S_{\text{SO}_2}^0 = -61,24$ kal/mol · grad; 400 K da hisoblash uchun (Temkin-Shvarsman usuli bo'yicha)
 $M_0 = 0,0392$, $M_1 = 0,030 \cdot 10^3$, $M_2 = 0,0364 \cdot 10^{-5}$.

47. 1000°C (1273 K) da:



reaksiyaning muvozanat konstantasi K_p ni aniqlang. Buni yechishda quyida keltirilgan ma'lumotlardan foydalaning:

$$\left(\frac{G^0 - H^0}{T} \right) \text{CO} = -210,939 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{0,\text{CO}}^0 = -113,880 \text{ kJ/mol} \cdot \text{grad};$$

$$\left(\frac{G^0 - H_0}{T} \right)_{\text{H}_2} = -143,483 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298,\text{H}_2}^0 = 0 \text{ kJ/mol};$$

$$\left(\frac{G^0 - H_0}{T} \right)_{\text{CH}_4} = -211,123 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298,\text{CH}_4}^0 = -66,965 \text{ kJ/mol} \cdot \text{grad};$$

$$\left(\frac{G^0 - H_0}{T} \right)_{\text{CO}_2} = -235,990 \text{ J/mol} \cdot \text{grad};$$

$$\Delta H_{298,\text{CO}_2}^0 = -393,229 \text{ kJ/mol} \cdot \text{grad}.$$

KO'P VARIANTLI MASALALAR

1. Ikki usul bilan reaksiyalarning muvozanat konstantasi K_p ni aniqlang:

1) standart hosil bo'lish issiqlik effekti ΔH_{298}^0 va entropiyaning standart mutlaq (absolut) qiymatlari S_{298}^0 dan foydalanib;

2) keltirilgan izobarik potensial 1 atm. bosimdagi va mutlaq noldagi reaksiya effekti ΔH_0 dan foydalanib toping.

Kerakli ma'lumotlarni ilovadan oling. Agar kerakli haroratda ma'lumot berilmagan bo'lsa, uni ekstrapolatsiya (fikran davom ettirish yo'li) bilan topish mumkin. Barcha moddalarni gaz holatida deb hisoblang.

№	Reaksiya	T, K
1	2	3
1	$\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	500
2	$\text{C}_2\text{H}_6 + \text{CO} = \text{CH}_3\text{COCH}_3$	400
3	$\text{CH}_4 + \text{CO}_2 = \text{CH}_3\text{COOH}$	400
4	$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$	500
5	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	600
6	$\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{H}_2\text{O}$	500
7	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$	600
8	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$	500
9	$\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$	500
10	$\text{CO}_2 + 4\text{H}_2\text{O} = \text{CH}_4 + 2\text{H}_2\text{O}$	675
11	$\text{HCl} = 0,5\text{H}_2 + 0,5\text{Cl}_2$	400
12	$0,5\text{N}_2 + 0,5\text{O}_2 = \text{NO}$	1400
13	$\text{H}_2\text{O} = \text{H}_2 + 0,5\text{O}_2$	1000
14	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$	2000
15	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	1200
16	$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	900
17	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$	1000
18	$4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$	700
19	$\text{CO} + 3\text{H}_2\text{O} = \text{CH}_4 + \text{H}_2\text{O}$	1000
20	$3\text{CO} + 2\text{H}_2\text{O} = \text{CH}_3\text{OH} + 2\text{CO}_2$	1000

2. *A* va *B* moddalar stexiometrik miqdorda reaksiyaga kiritilgan. Umumiy bosim $1,0133 \cdot 10^5$ Pa va *T* haroratda *D* moddaning unumini aniqlang. Kerakli ma'lumotlarni ilovadan oling.

№	Реаксиya	A	B	C	D	$P \cdot 10^{-4}, \text{Pa}$				T, K
						A	B	C	D	
1	$\text{H}_2 + 0,5\text{O}_2 = \text{H}_2\text{O}$	H_2	O_2	—	H_2O	7	6	—	3	1000
2	$\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$	H_2	Cl_2	—	HCl	4	3	—	1,5	900
3	$2\text{HCl} + \text{O}_2 = \text{Cl}_2 + \text{H}_2\text{O}$	HCl	O_2	Cl_2	H_2O	4	3	1,5	1,5	1000
4	$0,5\text{N}_2 + 1,5\text{H}_2 = \text{NH}_3$	N_2	H_2	—	NH_3	10	15	—	10	600
5	$\text{N}_2 + \text{O}_2 = 2\text{NO}$	N_2	O_2	—	NO	4	1	—	1	1000
6	$\text{NO}_2 = \text{NO} + 0,5\text{O}_2$	NO_2	—	NO	O_2	6	—	2	3	400
7	$\text{N}_2\text{O}_4 = 2\text{NO}_2$	N_2O_4	—	—	NO_2	5	—	—	2	340
8	$\text{SO}_2 + 0,5\text{O}_2 = \text{SO}_3$	SO_2	O_2	—	SO_3	3	1	—	1,5	900
9	$\text{SO}_2 + \text{NO}_2 = \text{SO}_3 + \text{NO}$	SO_2	NO_2	SO_3	NO	6	3	1,5	1,2	700
10	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	CO	H_2O	CO_2	H_2	5	2	0,7	1,6	1000
11	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	CO	Cl_2	—	COCl_2	2	3	—	0,5	900
12	$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$	CO	H_2	—	CH_3OH	4	3	—	1,6	570
13	$\text{CO} + 0,5\text{O}_2 = \text{CO}_2$	CO	O_2	—	CO_2	4	6	—	3	1000
14	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$	CH_4	H_2O	CO	H_2	2	3	0,8	0,7	500
15	$3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$	C_2H_4	—	—	C_6H_6	2	—	—	3	780
16	$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$	C_2H_4	H_2	—	C_2H_6	7	8	—	3	780
17	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} = \text{C}_2\text{H}_5\text{OH}$	C_2H_4	H_2O	—	$\text{C}_2\text{H}_5\text{OH}$	3	2	—	1,2	480

V b o b

STATISTIK TERMODINAMIKA

Termodinamik kattaliklar ΔU , ΔH , ΔS , ΔF , ΔG va boshqa qiymatlarni statistik usul bilan ham hisoblash mumkin. Bunga holat yig'indisi (yoki holat funksiyasi) Z deb atalgan kattalikni aniqlash orqali erishiladi:

$$Z = \sum g_i e^{-E_i / RT} = \sum g_i e^{-(E_{il} + E_{ay} + E_{i,ay} + E_t + E_{el})}, \quad (V.1)$$

E_{il} , E_{ay} , $E_{i,ay}$, E_t , E_{el} — molekulaning ilgarilanma, aylanma, ichkari aylanma (molekuladagi bir atom guruhining boshqa guruhga nisbatan erkin aylanishi), tebranma elektronlar harakatlari energiyasi;

g_i — har qaysi harakat energiyasining umumiy yig'indidagi energiya ulushi: ko'p hollarda ikki atomli gazlar uchun $g_i = 1$ ga teng.

$$Z = Z_{il} \cdot Z_{ay} \cdot Z_{i,ay} \cdot Z_m \cdot Z_{el}, \quad (V.2)$$

Z_{il} , Z_{ay} , $Z_{i,ay}$, Z_t , Z_{el} lar holat yig'indisini tashkil qiluvchilar deyiladi.

Ilgarilanma harakat uchun Z_{il} :

$$Z = \frac{(2\pi k)^{3/2} \cdot RM^{3/2} T^{5/2} P^{-1}}{h^3 N^{5/2}} e,$$

bunda: h — Plank doimiysi; N — Avogadro doimiysi; P — bosim; T — mutlaq harorat; k — Bolsman doimiysi; M — molekular massa; e — natural logarifm asosi.

Bu tenglamaga turg'un kattaliklarning qiymatlari qo'yilsa va logarifmlansa:

$$\ln Z_{ii} = 3,4539 \lg M + 5,7565 \lg T - 2,3026 \lg P + 8,8612. \quad (\text{V.3})$$

Ikki atomli molekulaning aylanma harakati uchun Z_{ay} . (SI o'lchov sistemasida):

$$\ln Z_{ay} = 2,3026 \lg J + 2,3026 \lg T - 2,3026 \lg r - 104,5265, \quad (\text{V.4})$$

bunda: J — molekulaning inersiya momenti; δ — simmetriklik darajasi: gomoyadroli molekula uchun $\delta = 2$ va geteroyadroli molekula uchun $\delta = 1$.

Ko'p atomli molekulalarda bir-biriga nisbatan erkin aylanuvchi atom guruhi bor molekula uchun $Z_{i,a}$ (SI sistemada):

$$\ln Z_{i,a} = 1,1513 \lg J - 2,3026 \lg \delta + 1,1513 \lg T + 52,836. \quad (\text{V.5})$$

Ko'p atomli molekulalar uchun:

$$\ln Z = 0,5 \cdot 2,3026 \lg J + 3,4539 - 2,3026 \lg \delta - 157,3621. \quad (\text{V.6})$$

O'z navbatida J :

$$J = \mu r^2,$$

bunda: μ — keltirilgan massa va u

$$\mu = \frac{A \cdot B}{A + B} \cdot \frac{m_c}{12} \quad (\text{V.7})$$

ga teng.

Bunda: A, B — A va B atomlar yadrosi massasi; m_c — uglerod atomi yadrosi massasi, $19,95 \cdot 10^{-27}$ kg ($19,95 \cdot 10^{-24}$ g)ga teng, 12 — C^{12} uglerod izotopining atom massasi.

Bitta erkin darajali tebranma harakatli ikki atomli molekula uchun:

$$Z_m = \frac{1}{1 - e^{-hc\omega / kT}} = \frac{1}{1 - e^{-\theta / T}}. \quad (\text{V.8})$$

ω — tebranma harakatning takroriyligi, m^{-1} ; θ — tavsifiy harorat:

$$\theta = (hc\omega)k = 1,4387 \cdot 10^{-2}\omega. \quad (\text{V.9})$$

Ko'p atomli molekulalar uchun:

$$Z_m = \prod_{i=1}^{3n-5} \frac{1}{1 - e^{\theta_i / T}}.$$

Ikki atomli molekulalar elektron harakati Z_e uchun:

$$Z_e = g_{o,el} = 2S + 1, \quad (\text{V.10})$$

bunda: $g_{o,el}$ — nol elektron darajasining chetlanganligi (вырождение); S — molekuladagi elektron spinlar yig'indisi.

Elektronning energiya darajasi: $(2S + 1) M_B$, bunda: S — molekuladagi elektronlar spinlarining yig'indisi, M_B — elektronlar harakati momentlarining yig'indisi.

Termodinamik va fizik kattaliklar uchun Z orqali quyidagi ifodalar beriladi, masalan, ichki energiya qiymati nol energiya holatlaridan boshlab hisoblanadi:

$$U - U_0 = \Delta U; \quad \Delta U = RT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_v. \quad (\text{V.11})$$

Ichki energiyani ayrim harakatlarning energiyasidan foydalanib hisoblash qulayroqdir:

$$U = U_{il} + U_{ay} + U_{il} + U_{el} + U_t \quad (V.12)$$

$$U_{il} = 1,5RT. \quad (V.13)$$

Bitta erkinlik darajasi bo'lgan aylanma harakat uchun:

$$U_{i.a} = 0,5RT. \quad (V.14)$$

Ikki atomli molekula va bir chiziqli ko'p atomli molekula uchun U_i :

$$\frac{U - U_0}{T} = \frac{\frac{\theta}{R}}{\frac{\theta}{eT}} \quad (V.15)$$

ga teng.

θ/T — Eynshteynning termodinamik funksiyasi (chiziqli garmonik ossillator uchun) ma'lumotnomalarda berilgan. Ko'p atomli molekulalar uchun tebranma harakat energiyasi har qaysi erkinlik darajasi bo'yicha hisoblanib, ularning yig'indisi olinadi. Chiziq bo'ylab joylashgan ikki atomli molekula va ko'p atomli molekula uchun tebranma erkinlik darajalari:

$$f_i = 3n - 5,$$

chiziq bo'ylab joylashmaganlar uchun:

$$f_i = 3n - 6,$$

bunda: n — molekuladagi atomlar soni.

Ko'p atomli molekulalar uchun ichki energiyaning tebranma harakatini tashkil qiluvchisi — elementning tebranma harakat erkinlik darajasi uchun hisoblanib, so'ng ularning yig'indisi olinadi.

Gazlarning entropiyasi quyidagi tenglama bo'yicha topiladi:

$$S_T = R \ln Z + RT \left(\frac{\partial \ln Z}{\partial T} \right)_v \quad (\text{V.16})$$

entropiyani ayrim tashkil qiluvchilar entropiyasidan foydalanib topish qulayroq:

$$S_T = S_{il} + S_{ay} + S_{i,a} + S_t + S_{el} \quad (\text{V.17})$$

$$S_{il} = R \ln Z_{il} + 1,500 R \quad (\text{V.18})$$

$$S_{ay} = R \ln Z_{ay} + R \quad (\text{V.19})$$

$$S_{el} = R g_{o,el} \quad (\text{V.20})$$

bunda: $g_{o,el}$ — nol elektron darajasining chetlanganligi (вырождение); S_t — ma'lumotnomalarda Eynshteynning termodinamik funksiyasi orqali topiladi.

ΔU , S ma'lum bo'lsa, N , F , G , C_p larni hisoblash mumkin.

Ikki atomli gaz molekulalari uchun izoxorik issiqlik sig'imi C :

$$C_v = \left(\frac{dU}{dT} \right)_v = 2RT \left(\frac{d \ln Z}{dT} \right)_v + RT^2 \left(\frac{d^2 \ln Z}{dT^2} \right)_v.$$

Issiqlik sig'imini ham tashkil qiluvchi ayrim harakat issiqlik sig'imlaridan aniqlash qulayroq:

$$C_v = C_{il} + C_{ay} + C_t + C_{i,a}, \quad (\text{V.21})$$

$$C_{v,il} + C_{ay} = 2,5 R; \quad C_{v,il} = 1,5 R, \quad (\text{V.22})$$

$$C_{v,i.v.} = 0,5 R, \quad (V.23)$$

$$C_{v,t} = \frac{R \cdot \left(\frac{0}{T}\right)^2 e^{0/T}}{\left(e^{0/T} - 1\right)^2}. \quad (V.24)$$

$C_{v,t}$ qiymati ma'lumotnomalarda ma'lum. Q/T uchun Eynshteynning termodinamik funksiyasidan foydalanib aniqlanadi:

$$C_E = \frac{R \cdot \left(\frac{0}{T}\right)^2 \cdot e^{\frac{0}{T}}}{\left(e^{0/T} - 1\right)^2}. \quad (V.25)$$

MASALALAR YECHISHIGA DOIR MISOLLAR

1. CO ning 1, 0133 · 10⁵ Pa va 500 K da holatlar yig'indisining ilgari lanma tashkil qiluvchisini aniqlang.

Ye ch i sh. (V.3) tenglamaga CO ning massasi, bosim va harorat qiymatlari qo'yilsa:

$$\begin{aligned} \ln Z_{il} &= 3,4539 \lg 28 + 5,7565 \lg 500 - 2,3026 \lg 1,0133 \cdot 10^5 + \\ &+ 8,8612 = 4,9983 + 15,5365 - 11,5262 + 8,8612 = 17,8669 \\ \lg Z_{il} &= \frac{17,8669}{2,3} = 7,7607; \quad Z_{il} = 5,764 \cdot 10^7. \end{aligned}$$

2. CO ning 500 K da holatlar yig'indisining aylanma tashkil qiluvchisini aniqlang. CO ning inersiya momenti $J = 14,49 \cdot 10^{-47}$ kg · m² ga teng.

Ye ch i sh. CO geteroyadroli molekula bo'lganligi uchun $\tau = 1$ ga teng. (V. 4) tenglamaga bu ma'lumotlar qo'yib chiqilsa:

$$\ln Z_{ay} = 2,3026 \lg 14,49 \cdot 10^{-47} + 2,3026 \lg 500 - 2,3026 \lg 1 +$$

$$+ 104,5265 = -105,5487 + 6,2146 + 104,5265 = 5,1924,$$

$$\lg Z_{ay} = \frac{5,1924}{2,3} = 2,2550, \quad Z_{ay} = 179,9.$$

3. CO ning 500 K da holatlar yig'indisining tebranma harakat tashkil qiluvchi qismini aniqlang. Harakat takroriyliigi $2,170 \cdot 10^5 \text{ m}^{-1}$.

Yechish. (V.6) tenglamadan foydalanish uchun keltirilgan haroratda θ ning qiymatini (V.7) tenglamadan topamiz:

$$\theta = 1,4387 \cdot 10^{-2} \omega = 1,4387 \cdot 10^{-2} \cdot 2,170 \cdot 10^5 = 3123,$$

$$\theta/T = 3123/500 = 6,245.$$

(V.6) tenglama bo'yicha Z_m ni topamiz:

$$Z_m = \frac{1}{1 - e^{\theta/R}} = \frac{1}{1 - e^{-6,245}} = 1,0019.$$

4. $1,0133 \cdot 10^5 \text{ Pa}$ bosimda va 500 K da CO ning holatlar yig'indisini aniqlang.

Yechish. (V.2) tenglamaga muvofiq:

$$Z = Z_{il} \cdot Z_{ay} \cdot Z_{i,a} \cdot Z_m \cdot Z_{el} = 5,764.$$

CO elektron spinlarining yig'indisi nolga teng bo'lganligidan yig'indi holatning elektron tashkil qiluvchisi $Z_{el} = 0$ ga teng. Ikki atomli molekulada ichki aylanma harakatning erkinlik darajasi yo'q, demak, $Z_{i,a} = 0$. Bunday holda (V.2) tenglama:

$$Z = 5,764 \cdot 10^7 \cdot 1,0019 = 1,0389 \cdot 10^{10}.$$

5. 500 K da CO ichki energiyasining ilgarilanma harakat tashkil qiluvchisini aniqlang.

Y e c h i s h . Ilgarlanma harakatning ichki energiyasini tenglama (V.II) dan foydalanib topamiz:

$$I_{il} = 1,5RT = 1,5 \cdot 8,3143 \cdot 500 = 6,2357 \cdot 10^3 \text{ J/mol.}$$

6. 500 K da CO ning ichki energiya aylanma harakat tashkil qiluvchisini aniqlang.

Y e c h i s h . Aylanma harakat tashkil qiluvchisi (V.12) tenglama bo'yicha aniqlanadi. CO molekulasida ikki erkinlik darajali aylanishda bo'ladi:

$$I_{ay} = 2 \cdot 0,5RT = 2 \cdot 8,3143 \cdot 500 = 4,1571 \cdot 10^3 \text{ J/mol.}$$

7. 500 K da CO ichki energiyasining tebranma harakat tashkil qiluvchisini aniqlang. $\theta/T = 6,245$ ga teng.

Y e c h i s h . I_i ni (V.14) tenglamaga muvofiq:

$$\left(\frac{U - U_0}{T} \right)_{ay} = \frac{R^{0/T}}{e^{\frac{\theta}{T}} - 1}$$

$\frac{\theta}{T}$ ga bog'liq bo'lgan $\frac{U - U_0}{T}$ ni Eynshteynning termodinamik funksiyasidan topamiz:

$\frac{\theta}{T}$	6,00	6,40
$\frac{U - U_0}{T}$	0,1243	0,1050

bundan:

$$\Delta \frac{\theta}{T} = 6,40 - 6,00 = 0,40;$$

$$\Delta \frac{U - U_0}{T} = 0,1243 - 0,1050 = 0,0193 \text{ J/mol} \cdot \text{grad};$$

$$0,40 - \frac{0,0193}{0,245} \Big\} \rightarrow x = \frac{0,245 \cdot 0,0193}{0,40} = 0,0118;$$

$$\frac{U - U_0}{T} = 0,1243 - 0,0118 = 0,1125 \text{ J/mol} \cdot \text{grad};$$

$$(U - U_0) = 0,1125 \cdot 500 = 0,0562 \cdot 10^3 \text{ J/mol}.$$

8. 500 K da CO ning ichki energiyasini aniqlang.

Yechish. $U_{el} = 0$. $U_{i.ay.} = 0$ ga teng. CO molekulasida ichki aylanish erkinlik darajasi yo'q $U_{i.ay} = 0$, shunga ko'ra (V.10) tenglamaga muvofiq: $(U - U_0) = 6,2357 \cdot 10^3 + 4,1571 \cdot 10^3 + 0,0562 \cdot 10^3 = 10,449 \cdot 10^3 \text{ J/mol}$.

9. 500 K harorat va $1,0133 \cdot 10^5 \text{ N/m}^2$ bosimda metanolning ichki energiyasini aniqlang.

Yechish. Ko'p atomli molekulalar uchun ilgarilanma harakatning ichki energiyasini hisoblash ikki atomli molekulalar uchun hisoblashdan farq qilmaydi. Shunga ko'ra, (V.II) tenglama bo'yicha:

$$U_{il} = 1,5RT = 1,5 \cdot 8,3143 \cdot 500 = 6,2357 \cdot 10^3 \text{ J/mol}.$$

Metanol molekulasi aylanma harakatda uchta erkinlik darajasiga ega va shu sababdan (V.12) tenglamaga muvofiq:

$$U_{ay} = 3 \cdot 0,5RT = 1,5 \cdot 8,3143 \cdot 500 = 6,2357 \cdot 10^3 \text{ J/mol}.$$

Metanol molekulasi ichki aylanma harakatda bitta erkinlik darajasiga ega. Shunga ko'ra, (V.13) tenglamaga muvofiq:

$$U_{i.ay} = 0,5 \cdot 8,3143 \cdot 500 = 2,0785 \cdot 10^3 \text{ J/mol}.$$

Metanol molekulasiining tebranma harakati 2 ta erkinlik darajasiga ega. Shunga ko'ra, energiyani 2 ta erkinlik darajasi bo'yicha tebranma harakatini jamlash kerak. Kerakli ma'lumotlar (T qiymati va bunga to'g'ri kelgan $\frac{\theta}{T}$ qiymatlar) ma'lumotnomalarda — garmonik ossillator uchun Eynshteynning termodinamik funksiyalari jadvalidan olinadi. U_T (V.14) tenglama asosida topiladi:

$$(U - U_0) = \left(\frac{U - U_0}{T} \right) \cdot 500 = 6,7281 \cdot 500 = 3,364 \cdot 10^3 \text{ J/mol}$$

va

$$(U - U_0)_{500} = 6,2357 \cdot 10^3 + 6,2357 \cdot 10^3 + 2,0785 \cdot 10^3 + 3,3640 \cdot 10^3 = 17,9139 \cdot 10^3 \text{ J/mol.}$$

$\omega \cdot 10^{-5}, \text{ m}^{-1}$	chetlan- ganlik	$\theta / 500,$ $\text{J/mol} \cdot \text{grad}$	$\left(\frac{U - U_0}{T} \right), \text{J/mol} \cdot \text{grad}$	$C_E,$ $\text{J/mol} \cdot \text{grad}$
3,683		10,598	0,0023	0,023
2,976	2	8,564	0,0143	0,118
2,843		8,187	0,0193	0,158
1,455	2	4,187	0,537	2,283
1,340		3,859	0,693	2,750
1,116	2	3,211	1,121	3,751
1,031		2,967	1,338	4,186

10. 500 K harorat va $1,0133 \cdot 10^5 \text{ Pa}$ bosimda CO ning entropiyasini aniqlang.

Y e c h i s h . (V.15) tenglamadan foydalanib aniqlanadi:

$$S_T = R \ln Z + RT \left(\frac{\partial \ln Z}{\partial T} \right)_v.$$

Ayrim harakatlarning entropiyasini aniqlab, so'ng ular jamlanadi.

$$(V.16) \text{ bo'yicha: } S = S_{il} + S_{ay} + S_t + S_{el}.$$

Oldin Z_{il} qiymati aniqlanadi, Z_{il} ning qiymati (V.3) tenglamadan aniqlanadi va $\left(\frac{\partial \ln Z}{\partial T}\right)_v$ hosilasi olinadi. Natijada $1,5 \cdot \frac{1}{T}$ ga teng bo'ladi.

$$S_{il} = R \ln Z_{il} + 1,500 R,$$

$$S_{il} = 3,4539 \lg 28 + 5,756 \lg 500 - 2,3026 \lg 1,0133 \cdot 10^3 + \\ + 8,8612 + 1,500 \cdot 8,3143 = 161,0472 \text{ J/mol} \cdot \text{grad}.$$

S_{ay} qiymatini (V.18) tenglamadan topamiz, $\ln Z_{ay}$ — harakat entropiyasi qiymati (V.4) dan topiladi va so'ng $\left(\frac{\partial \ln Z}{\partial T}\right)_v$ hosilasi olinadi, natijada:

$$S_{il} = 3,4539 \lg 28 + 5,7565 \lg 500 - 2,3026 \lg 1,0133 \cdot 10^3 + \\ + 8,8612 + 1,500 \cdot 8,3143 = 161,0472 \text{ J/mol} \cdot \text{grad}.$$

Bu $1,5 \cdot \frac{1}{T}$ ga teng. (V.18) tenglama $S_{ay} = R \ln Z_{ay} + R$ tenglamasi olinadi. CO uchun $J = 14,49 \cdot 10^{-47} \text{ kg/m}^2$ va $\delta = 1$ ga teng.

$$S_{ay} = 2,3026 \ln 14,49 \cdot 10^{-47} + 2,3026 \\ \lg 500 + 104,5263 + 1,0508 \cdot 8,3143 = 51,4854 \text{ J/mol} \cdot \text{grad}.$$

S_t ning qiymati θ/T asosida ma'lumotnomalardan Eynshteynning termodinamik funksiyasidan hisoblab aniqlanadi: $\theta/T = 6,245$ ga teng.

$$\theta/T = 6,00 = 6,40 \\ S_t = 0,146 = 0,100$$

Bu jadvaldan $\Delta \frac{\theta}{T} = 0,40$; $S_f = 0,146$; $\theta/T = 6,245$ ga tengligidan:

$$\left. \begin{array}{l} 0,40 - 0,046 \\ 0,245 - x \end{array} \right\} x = 0,028,$$

bundan

$$S_f = 0,146 - 0,028 = 0,118 \text{ J/mol} \cdot \text{grad}.$$

CO da elektronlar spinlari yig'indisi nolga teng, demak, $S_{el} = 0$ bo'ladi. CO ning entropiyasi barcha harakat entropiyalari yig'indisiga teng:

$$\begin{aligned} S &= S_{il} + S_{ay} + S_f = 161,0472 + 51,4854 + 0,118 = \\ &= 212,6506 \text{ J/mol} \cdot \text{grad}. \end{aligned}$$

11. 500 K da CO ning turg'un hajmdagi issiqlik sig'imini ilgariylanma harakatga mansub qismi $C_{v,il}$ ni aniqlang.

Yechish. (V.20) tenglamaga muvofiq:

$$C_{v,il} = 1,5 R = 1,5 \cdot 8,3143 = 12,4715 \text{ J/mol} \cdot \text{grad}.$$

12. 500 K da turg'un hajmdagi issiqlik sig'imining aylanma harakatga to'g'ri keladigan tashkiliy qismi $C_{v,ay}$ miqdorini aniqlang.

Yechish. CO molekulasining aylanma harakati ikkita erkinlik darajasiga teng.

(V.21) tenglamaga muvofiq:

$$C_{v,ay} = 2 \cdot 0,5 \cdot 8,3143 = 8,3143 \text{ J/mol} \cdot \text{grad}.$$

13. 500 K da CO ning turg'un hajmdagi issiqlik sig'imining tebranma harakatga to'g'ri kelgan qismi $C_{v,t}$ ni aniqlang.

$\theta/T = 6,245$ ga teng.

Yechish. $C_{v,t}$ ning qiymati ma'lumotnomalarda berilgan Eynshteynning termodinamik funksiyasidan foydalanib aniqlanadi:

$$\begin{aligned}\theta/T &= 6,00 - 6,40 \\ S_{v,t} &= 0,745 - 0,569.\end{aligned}$$

Chiziqli interpolatsiyadan foydalanib quyidagilarni aniqlaymiz:

$$\left. \begin{aligned}0,40 - 0,176 \\ 0,245 - x\end{aligned} \right\} x = 0,1078.$$

Demak, $C_{v,t} = 0,745 - 0,108 = 0,6377 \text{ J/mol} \cdot \text{grad}$ (yoki jadvalga ko'ra C_E funksiya).

CO ning 500 K izoxorik issiqlik sig'imi C_v :

$$\begin{aligned}C_v &= C_{v,il} + C_{v,ay} + C_{v,t} = 12,4715 + 8,3143 + 0,637 = \\ &= 21,4228 \text{ J/mol} \cdot \text{grad ga teng bo'ladi.}\end{aligned}$$

14. CO ning 500 K va $1,0133 \cdot 10^5 \text{ Pa}$ bosimdagi izobarik issiqlik sig'imi C_p ni aniqlang.

Yechish. $C_p = C_v + R = 21,4228 + 8,3143 = 29,7371 \text{ J/mol} \cdot \text{grad}.$

MASALALAR

1. 298 K va $1,0133 \cdot 10^5 \text{ Pa}$ bosimda F_2 ning holat yig'indisi ilgarilanma tashkil qiluvchisi Z_{il} ni aniqlang.

2. 298 K da F_2 ning holat yig'indisi aylanma tashkil qiluvchisi Z_{ay} ni aniqlang. Kerakli ma'lumotlar ma'lumotnomalardan olingan.

3. 298 da F_2 ning holat yig'indisi tebranma tashkil qiluvchisi Z_t ni aniqlang. Kerakli ma'lumotlarni ma'lumotnomalardan oling.

4. 298 K da F_2 ning holat yig'indisi elektron tashkil qiluvchisi Z_{el} ni aniqlang. Kerakli ma'lumotlarni ma'lumotnomalardan oling.
5. 298 K da va $1,0133 \cdot 10^5$ Pa bosimda F_2 ning holat yig'indisini aniqlang. Kerakli ma'lumotlarni ma'lumotnomalardan oling.
6. F_2 ning 298 K da va $0,5 \cdot 10^5$ Pa bosimdagi holat yig'indisini aniqlang. Kerakli ma'lumotlarni ma'lumotnomadan oling.
7. F_2 ning 1000 K va $1,0133 \cdot 10^5$ Pa dagi holat yig'indisini aniqlang. Kerakli ma'lumotlarni ma'lumotnomadan oling.
8. 100 K da va $1,0133 \cdot 10^5$ Pa da HJ ning holat yig'indisini aniqlang. Kerakli ma'lumotlarni ma'lumotnomadan oling.
9. 1000 K da O_2 ning ichki energiyasi tashkil qiluvchisi ilgarilanma harakat energiyasi U_{il} ni aniqlang.
10. 1000 K da O_2 ning ichki energiyasi aylanma harakat tashkil qiluvchisi U_{ay} ni aniqlang.
11. 1000 K da O_2 ning ichki energiyasi tebranma harakat tashkil etuvchisi U_m ni aniqlang.
12. 1000 K da va $1,0133 \cdot 10^5$ Pa bosimda O_2 ning ichki energiyasini aniqlang. Kerakli ma'lumotlarni ma'lumotnomadan oling.
13. 298 K da va $1,0133 \cdot 10^5$ Pa da kriptonning ichki energiyasi va entropiyasini aniqlang. Holat yig'indisining elektron harakat tashkil qiluvchisi $Z_{el} = 0$.
14. 500 K da kislorod entropiyasi aylanma harakat tashkil etuvchisi S_{ay} ni aniqlang. Yadrolar oralig'i $1,207 \cdot 10^{-10}$ m.
15. 298 K, 1000 K va 3000 K da CO entropiyasi tebranma harakat tashkil etuvchisi S_t ni aniqlang. Tebranish takroriyligi $2,170 \cdot 10^5$ m $^{-1}$.
16. 298 K va $1,0133 \cdot 10^5$ Pa da NO ning entropiyasini aniqlang. Yadrolar oralig'i $1,15 \cdot 10^{-5}$ m, tebranish takroriyligi $1,9165 \cdot 10^5$ m $^{-1}$ holat yig'indisi elektron tashkil etuvchisi 4 ga teng.
17. 1000 K da metanning izoxorik issiqlik sig'imi C_v holat yig'indisi ilgarilanma tashkil qiluvchisi $C_{v,il}$ ni aniqlang.

18. 1000 K da metanning izoxorik issiqlik sig'imi holat yig'indisi aylanma tashkil qiluvchisi $C_{v,ay}$ ni aniqlang.

19. 1000 K da metanning izoxorik issiqlik sig'imi tebranma tashkil qiluvchisi $C_{v,t}$ ni aniqlang. Tebranish chetlanishlari $\nu_s \sim 1$, $\nu_{as} \sim 3$, $\delta_s \sim 2$, $\delta_{as} \sim 3$ ga teng.

KO'P VARIANTLI MASALALAR

1. Ideal gaz holatida turgan A moddaning T_1 , T_2 va T_3 harorat va $1,0133 \cdot 10^5$ Pa bosimdagi quyidagi kattaliklarini aniqlang:

1) holat yig'indisini; ilgarilanma, aylanma va tebranma tashkil qiluvchilarni; 2) holat yig'indisini; 3) ichki energiyaning ilgari-
lanma, aylanma va tebranma tashkil qiluvchilarini; 4) ichki energiyaning holat yig'indisini; 5) izoxorik issiqlik sig'imi C_v ilgarilanma, aylanma va tebranma tashkil qiluvchilarini; 6) issiqlik sig'imi C_p ni; 7) entropiyaning ilgarilanma, aylanma va tebranma harakat tashkil qiluvchilarini; 8) entropiya S_f ni.

No	Modda	T_1	T_2	T_3
1	$^{79}\text{Br} - ^{79}\text{Br}$	300	500	1000
2	$^{79}\text{Br} - ^{79}\text{Br}$	300	600	900
3	$^{12}\text{C} - ^{16}\text{O}$	200	400	800
4	$^{13}\text{C} - ^{16}\text{O}$	300	600	1000
5	$^{35}\text{Cl} - ^{35}\text{Cl}$	400	800	1000
6	$^{35}\text{Cl} - ^{19}\text{F}$	300	600	1000
7	$^{19}\text{F} - ^{19}\text{F}$	200	500	1200
8	$^2\text{H} - ^2\text{H}$	200	400	900
9	$^1\text{H} - ^1\text{H}$	300	600	1000
10	$^2\text{H} - ^3\text{H}$	300	500	900
11	$^3\text{H} - ^3\text{H}$	400	600	1200
12	$^1\text{H} - ^3\text{H}$	300	500	1000
13	$^1\text{H} - ^{79}\text{Br}$	400	600	1200

2. T harorat va $1,0133 \cdot 10^5$ Pa bosimda A modda uchun quyidagi kattaliklarni aniqlang (jadvalga qarang): 1) ichki energiya ($U - U_0$), 2) issiqlik sig'imi (C_v, C_p), 3) entropiya (S_T^0). Molekulaning geometrik parametrlari, tebranish takroriyliklari, chetlanish darajalari to'g'risidagi ma'lumotlarni ma'lumotnomadan oling.

Variantlar	A modda	T	Variant	A modda	T
1	CO_2	300	7	BeCl_2	400
2	CS	400	8	BH_3	300
3	N_2O	300	9	AlCl_3	400
4	SO_2	300	10	AlBr_3	1000
5	NH_3	400	11	Br_2	900
6	C_2H_2	200	12	HBr	1000

VI bob

ERITMALAR

VI.1. ERITMA TURLARI VA KONSENTRATSIYALAR

Bir (yoki bir qancha) moddaning boshqa bir (yoki bir qancha) moddalar ichida bir tekis tarqalishidan hosil bo'lgan sistemaga **eritma** deyiladi. Barcha eritmalar o'zidan elektr oqimini o'tkazishiga ko'ra ikki sinfga bo'linadi: **elektrolitlar** va **noelektrolitlar**. Noelektrolit eritmalariga ko'proq o'zidan elektr oqimini o'tkazmaydigan organik moddalar eritmasi kiradi. Elektrolit eritmalar o'zidan elektr oqimini yaxshi o'tkazadi va bu xil eritmalariga kislota, asos hamda tuzlarning suvdagi eritmasi va ularning suyuqlanmalari kiradi. Suyuqlanmalar erituvchi va eruvchi (yoki erigan) moddadan tashkil topadi. Erish jarayonida o'z agregat holatini saqlab qolgan modda shartli ravishda erituvchi hisoblanadi. Oddiy sharoitda qattiq holatda bo'lib (masalan, tuz, metall, metall oksidlari), ularning aralashmasi qizdirilib suyuqlikka aylantirilganda hosil bo'lgan eritma yana sovitilganda birinchi navbatda kristallangan (yoki cho'kmaga tushgan) modda eruvchi hisoblanadi.

Eritmalarning xossalari ularni hosil qilgan moddalarning (eruvchi va erituvchi) tabiati va miqdoriga bog'liq.

Eritmalar tarkibi konsentratsiya ifodasi orqali ko'rsatiladi. *Eritma yoki erituvchining ma'lum og'irlik miqdori yoki hajmida erigan modda miqdoriga konsentratsiya deyiladi.* Konsentratsiya — ikki xil usul bilan: og'irlik va hajmiy usulda ifodalanadi. Bir usuldan ikkinchi usulga o'tish kerak bo'lsa, u holda eritma zichligi (d) ma'lum bo'lishi shart. Eritma zichligi $d = \frac{m}{V}$ ga teng.

Hajm usulida molar (C) va normal (n) konsentratsiya, og'irlik usulida esa foiz (%), molal (m), molar qism (N) konsentratsiya ifodalari mavjud. Molar konsentratsiya — 1 litr (l) eritmada erigan moddaning mol soniga teng. Normal konsentratsiya — 1 litr eritmada erigan moddaning gramm-ekvivalent soniga teng (SI sistemasida kg/m^3). Foiz (%) konsentratsiya esa 100 gramm eritmada erigan moddaning gramm sonlariga teng. Molal konsentratsiya — 1000 gramm erituvchida erigan moddaning mol soniga teng.

Fizikaviy kimyoda ko'pincha molar qisim (mol foizi) ifodasidan foydalaniladi. Agar $n_1, n_2, n_3 \dots n_i$ lar 1,2,3... i = moddalarning mol sonlari bo'lsa, i = komponentning molar qismi

$$N_i = \frac{n_i}{\sum n_i} \quad (\text{VI.1})$$

ga teng bo'ladi.

Masalan, A va B moddalardan iborat bo'lgan eritmadagi A moddaning molar qismi N_A teng:

$$N_A = \frac{n_A}{n_A + n_B},$$

bunda A moddaning molar qismi N_A ; n moddalarning mol sonlari doimo $\sum N_i = 1$ bo'ladi.

Agar $N_i = 100 \cdot N_i$ bo'lsa, mol foiz bo'ladi.

Bundan:

$$N_i = \frac{n_i}{\sum n_i} \cdot 100 \text{ va foiz ifodasida } \sum N_i = 100 \text{ bo'ladi.}$$

KONSENTRATSIYA IFODASINI ANIQLASHGA DOIR MISOLLAR

1. 298 K da 10% li CaCl_2 eritmasining zichligi $1,22 \text{ g/sm}^3$ ga teng. Eritma tarkibini molar qism (N), molal (m), molar (C), normal (n) konsentratsiyalar orqali ifodalang.

Y e c h i s h . a) eritma molar qismi — $N_i = \frac{n_i}{\sum n_i}$.

Konsentratsiyaning bir ifodasidan boshqa ifodalariga o'tilganda, avval eritmaning gramm (g) va mol soni (n) bilan ifodalangan tarkibini aniqlash kerak. $g \rightleftharpoons n$ ga o'tishda:

$$n = \frac{g}{M} = \frac{\text{moddaning gramm miqdori}}{\text{moddaning molekular massasi}}$$

tenglamasidan foydalaniladi:

$$M_{\text{CaCl}_2} = 40,1 + 2 \cdot 35,46 = 111,02 \approx 111$$

$$M_{\text{H}_2\text{O}} = 2 + 16 = 18$$

10% li eritmada 10 g CaCl_2 va 90 g suv bor:

$$n_{\text{CaCl}_2} = \frac{10}{111} = 0,0901 \text{ mol}; \quad n_{\text{H}_2\text{O}} = \frac{90}{18} = 5 \text{ mol}.$$

Demak,

$$n_{\text{NaCl}_2} = \frac{0,0901}{0,0901+5} = 0,0177.$$

$\sum N_i = 1$ ga teng bo'lganligidan:

$$N_{\text{H}_2\text{O}} = 1 - 0,0177 = 0,9823 = 0,9823;$$

b) molal konsentratsiya (m):

0,0901 mol CaCl_2 — 90 g suvda
 m mol — 1000 g suvda

$$m = \frac{0,0901 \cdot 1000}{90} = 1;$$

d) molar konsentratsiyani aniqlash uchun $d = \frac{m}{V}$ yordamida massa sistemasidan hajm sistemasiga o'tish kerak, ya'ni 100 g eritma qancha hajmni ishg'ol qilishini bilish kerak:

$$V = \frac{m}{d} = \frac{100}{1,22} = 81,967 \text{ sm}^3.$$

Demak, 0,0901 mol CaCl_2 — 81,967 sm^3 eritmada,
 C — 1000 sm^3 eritmada esa

$$C = \frac{0,0901 \cdot 1000}{81,967} = 1,099;$$

e) normal konsentratsiya quyidagicha aniqlanadi: CaCl_2 tuzida 1 mol 2 gramm-ekivalentga teng bo'lganligidan:

$$n = 2 \cdot 1,099 = 2,198.$$

2. 298 K da 0,0177 molar qismga teng bo'lgan CaCl_2 ning suvdagi eritmasining zichligi 1,22 g/ sm^3 ga teng. Eritma tarkibini foiz (%), molal, molar va normal konsentratsiyalar bilan ifodalang.

Yechish. Tarkibiy qismlarning mol va gramm miqdorini quyidagicha aniqlash mumkin:

$$a) 0,0177 = \frac{n_{\text{CaCl}_2}}{n_{\text{CaCl}_2} + n_{\text{H}_2\text{O}}} \quad \text{va} \quad 0,9823 = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{CaCl}_2}} \quad \text{tenglamalarni}$$

yechib n_{CaCl_2} va $n_{\text{H}_2\text{O}}$, so'ngra $g = nM$ tenglamasidan foydalanib, eritmaning gramm bilan ifodalangan tarkibini aniqlash mumkin;

b) (qulayroq usul) tarkibiy qismlarning bittasi mol qiymatini (n) yuqoridagi tenglamalarning birortasiga qo'yib, ikkinchi moddaning mol miqdorini aniqlash mumkin. Faraz qilaylik, suvning mol miqdori 100 g eritmada, ya'ni:

$$n_{\text{H}_2\text{O}} = \frac{100}{18} = 5,55 \text{ bo'ladi.}$$

Unda

$$0,0177 = \frac{n_{\text{CaCl}_2}}{n_{\text{CaCl}_2} + n_{\text{H}_2\text{O}}} \quad \text{tenglamasidan}$$

$$n_{\text{CaCl}_2} = \frac{n_{\text{H}_2\text{O}} \cdot N_{\text{CaCl}_2}}{1 - N_{\text{CaCl}_2}} = \frac{0,0177 \cdot 5,55}{0,9823} = 0,1$$

va

$$g_{\text{CaCl}_2} = 0,1 \cdot 111 = 11,1,$$

$$g = 5,55 \cdot 18 = 100.$$

Molal konsentratsiya (m):

$$0,1 \text{ mol CaCl}_2 - 100 \text{ g suvda,}$$

$$m \text{ mol} - 1000 \text{ g suvda}$$

$$m = \frac{0,1 \cdot 1000}{100} = 1.$$

Foiz konsentratsiyada (%):

$$\text{Eritma massasi} = 100 + 11,1 = 111,1 \text{ g.}$$

$$111,1 \text{ g eritmada} - 11,1 \text{ g CaCl}_2$$

$$100 \text{ g eritmada} - \% \text{ CaCl}_2$$

$$\% = \frac{100 \cdot 11,1}{111,1} = 10\%.$$

Molar konsentratsiya (C) ni aniqlashda eritmaning hajmi aniqlanadi, ya'ni:

$$V = \frac{g}{d} = \frac{111,1}{1,22} = 91,005 \text{ sm}^3.$$

91,005 sm³ eritmada — 0,1 mol CaCl₂,
1000 sm³ eritmada — C mol CaCl₂ bor,

$$C = \frac{0,1 \cdot 1000}{91,005} = 1,098 \text{ mol.}$$

Normal konsentratsiya (n) quyidagicha hisoblanadi:

$$n = 2C = 2 \cdot 1,098 = 2,196.$$

3. 298 K da 0,098 molal konsentratsiyali CaCl₂ eritmasining zichligi 1,22 g/sm³ ga teng. Eritmaning molar qismi, foiz, molar va normal konsentratsiya ifodalarini aniqlang.

Yechish. Misolni yechish uchun CaCl₂ va suv miqdorini mol hamda gramm bilan ifodalash kerak. Masala shartiga ko'ra, eritma 0,098 mol CaCl₂ va 1000 g suvdan iborat. 1000 g suvning miqdori $n_{\text{H}_2\text{O}} = \frac{1000}{18} = 55,5 \text{ mol}$. CaCl₂ ning gramm miqdori $n = \frac{g}{M}$ dan kelib chiqib:

$$g_{\text{CaCl}_2} = nM = 0,098 \cdot 111 = 108,78 \text{ g.}$$

$$\text{Molar qismi } N_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{CaCl}_2}} = \frac{55,5}{55,5 + 0,098} = 0,998 \text{ va}$$

$$N_{\text{CaCl}_2} = 1 - N_{\text{H}_2\text{O}} = 1 - 0,998 = 0,002.$$

Foiz konsentratsiya (%):

Eritma massasi $m = 1000 \text{ g}$, suv + 108,78 g, CaCl₂ = 1108,78 g
1108,78 g eritmada — 108,78 g CaCl₂ bor,

100 g da — % CaCl₂

$$g = \frac{108,78 \cdot 100}{1108,78} = 10\%.$$

Molar konsentratsiya:

Oldin eritma hajmi aniqlanadi:

$$d = \frac{m}{V} \text{ dan } V = \frac{m}{d} = \frac{1108,78}{1,22} = 908,8 \text{ sm}^3.$$

908,8 sm³ eritmada — 0,098 mol CaCl₂

1000 sm³ eritmada — C mol CaCl₂

$$C = \frac{0,098 \cdot 1000}{908,8} = 1,078.$$

Normal konsentratsiya:

$$n = 2C = 2 \cdot 1,078 = 2,156.$$

4. 15°C da 2,31 mol/l molar konsentratsiyali H₂SO₄ ning zichligi 1,145 g/sm³ ga teng. Eritma tarkibini normal, molar qism, molal, foiz konsentratsiyalarda ifodalang.

Yechish. Eritma tarkibining gramm (g) va mol soni (n) miqdorlarini aniqlaymiz.

$$\text{Eritma massasi } m = V \cdot d = 1000 \cdot 1,145 = 1145 \text{ g.}$$

$$g_{\text{H}_2\text{SO}_4} = n \cdot M = 2,31 \cdot 98 = 226,38 \text{ g,}$$

$$g_{\text{H}_2\text{O}} = 1145 - 226,38 = 918,62 \text{ g,}$$

$$n_{\text{H}_2\text{SO}_4} = 2,31 \text{ mol/l, } n_{\text{H}_2\text{O}} = \frac{918,62}{18} = 51,0 \text{ mol/l,}$$

$$N_{\text{H}_2\text{SO}_4} = \frac{2,31}{2,31+51,0} = 0,043, \quad N_{\text{H}_2\text{O}} = 1 - 0,043 = 0,957 \text{ mol/l.}$$

Molal konsentratsiyada (m):

$$918,2 \text{ g suvda} — 2,31 \text{ mol H}_2\text{SO}_4$$

$$1000 \text{ g suvda} — m \text{ mol H}_2\text{SO}_4$$

$$m = \frac{2,31 \cdot 1000}{918,2} = 2,52 \text{ mol.}$$

Foiz konsentratsiyada (%):

$$1145 \text{ g eritmada} — 226,38 \text{ g H}_2\text{SO}_4$$

$$100 \text{ g eritmada} — \% \text{ H}_2\text{SO}_4$$

$$\% = \frac{226,38 \cdot 100}{1145} = 19,77\%.$$

Normal konsentratsiyada (n):

$$n = 2C = 2 \cdot 2,31 = 4,62.$$

VI.2. PARSIAL MOLAR KATTALIKLAR

Eritmalarning xossalari ularning tarkibiy qismlari (tashkil etuvchi komponentlar) tabiatiga va miqdoriga, ya'ni eritmaning tarkibiga bog'liqligini o'rganishda termodinamika usullaridan foydalaniladi. Eritma xossasi uning tarkibiy qismlari (komponentlar)ning eritmadagi xossalarining parsial molar kattaliklari yig'indisiga teng deb qabul qilingan. Eritmaning ekstensiv (miqdorga bog'liq bo'lgan xossalari) termodinamik xossalari — entalpiya (ΔH), entropiya (ΔS), izoxorik potensial (I), izobarik potensial (G), mol hajm (V) va hokazo eritmani tashkil qilgan modda (komponent)larning xossalari va miqdoriga bog'liqligini o'rganishda parsial mol kattaliklar ifodasidan foydalaniladi.

i moddaning parsial molar kattaligi turg'un harorat va bosimda eritmaga i komponentdan cheksiz kichik miqdorda qo'shilgandagi eritma xossasining cheksiz kichik o'zgarishiga yoki parsial molar kattalik — turg'un haroratda va bosimda juda katta hajmdagi eritmaga i komponentdan 1 mol qo'shilganda eritmaning ekstensiv xossasining o'zgarishiga tengdir.

Agar sistema ikki komponentli bo'lib, faqat bir erituvchi va bir eruvchidan iborat bo'lsa, eritmaning X xossasi erituvchi va eruvchilarning mol sonlari — n_1 , n_2 haroratga va bosimga bog'liq bo'ladi, ya'ni:

$$X = \varphi(T, P, n_1, n_2).$$

Ekstensiv xossa to'liq funksiya bo'lib, agar X hamma parametrlar bo'yicha $T = \text{const}$ va $P = \text{const}$ bo'lganida differensiallansa:

$$dX = \left(\frac{\partial X}{\partial n_1} \right)_{T, P, n_2} \cdot dn_1 + \left(\frac{\partial X}{\partial n_2} \right)_{T, P, n_1} \cdot dn_2. \quad (\text{VI.2})$$

Bunda

$$\left(\frac{\partial X}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_{i-1}} = X_i \quad \text{deb belgilasak,} \quad (\text{VI.3})$$

$$dX = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 \quad (\text{VI.4})$$

yoki

$$X_{um} = n_1 \bar{X}_1 + n_2 \bar{X}_2, \quad (\text{VI.5})$$

bunda: X_{um} — critmaning umumiy ekstensiv xossasi; $\bar{X}_i$ — i moddaning parsial molar kattaligi; 1—erituvchi, 2—eruvchi modda. Toza modda uchun parsial molar kattalik shu toza moddaning xossasiga teng:

$$\bar{X}_i = X_i^0. \quad (\text{VI.6})$$

Aralashtirish parsial molar funksiyasining o'zgarishi:

$$\Delta \bar{X}_i = \bar{X}_i - \Delta X_i^0, \quad (\text{VI.7})$$

bunda: $\Delta \bar{X}_i^0$ — 1 mol toza i moddaning xossasi; $\bar{X}_i$ — i moddaning critmadagi parsial kattaligi; $\Delta \bar{X}_i$ — i ta komponent parsial kattaliklarining crish jarayonidagi o'zgarishi.

Agar $\bar{X}_1, \bar{X}_2, n_1, n_2$ lar o'zgaruvchan miqdor deb, (VI.5) tenglama differensiallansa:

$$dX = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + (n_1 d\bar{X}_1 + n_2 d\bar{X}_2). \quad (\text{VI.8})$$

(VI.4) va (VI.8) tenglamalar o'zaro taqqoslansa:

$$n_1 d\bar{X}_1 + n_2 d\bar{X}_2 = 0. \quad (\text{VI.9})$$

Agar bu tenglamani $(n_1 + n_2)$ ga bo'lsak, $N_1 = -\frac{n_1}{n_1 + n_2}$ va $N_2 = \frac{n_2}{n_1 + n_2}$ c'tiborga olinsa, unda:

yoki

$$N_1 d\bar{X}_1 + N_2 d\bar{X}_2 = 0 \quad (\text{VI.10})$$

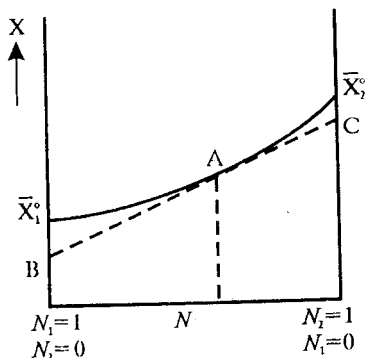
$$X_{um} = N_1 \bar{X}_1 + N_2 \bar{X}_2, \quad (\text{VI.11})$$

N — molar qism; X_{um} — 1 mol critmaning xossasi. Bu tenglamalar parsial molar kattaliklar molar qismini ifodalovchi Gibbs-Dyugem tenglamasi deyiladi. Komponentlardan bittasining parsial molar kattaligi ma'lum bo'lsa, bu tenglamalar yordamida ikkinchi moddaning parsial molar kattaligini hisoblash mumkin:

$$d\bar{X}_2 = -\frac{N_1}{N_2} d\bar{X}_1;$$

$$d\bar{X}_1 = -\frac{N_1}{N_2} d\bar{X}_2. \quad (\text{VI.12})$$

Parsial molar kattaliklarni grafik usul bilan aniqlash mumkin. Koordinatalarning ordinata o'qiga eritma xossasi (X), absissa o'qiga tarkib, ya'ni molar qismi (N) qo'yiladi (VI.1-rasm). Bu rasmdagi qalin



VI.1-rasm. Grafik usul bilan parsial molar kattaliklarni aniqlash.

egri chiziq eritma xossasining tarkib o'zgarishi bilan o'zaro bog'lanishini ko'rsatadi. Bu egri chiziqning istalgan nuqtasidan (masalan, A nuqtadan) urinma o'tkazib, uni ordinata o'qi bilan kesishguncha davom ettiriladi. Ordinata o'qining punktir chiziq bilan kesishgan nuqtasi (B, C nuqtalar) tegishli komponentning parsial molar kattaligi bo'ladi.

Agar eritma xossasi eritma tarkibi bilan quyidagicha bog'langan bo'lsa:

$$X_{um.} = N_1 X_1^0 + N_2 X_2^0.$$

Bu xossa additiv xossa deyiladi: X_1^0, X_2^0 — 1 mol toza moddaning xossasi.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. NaCl ning suvdagi eritmasi umumiy hajmi eritma tarkibi bilan quyidagicha bog'langan:

$$V_{um} = 55,55 \cdot V_{H_2O} + 16,4 m + 2,5 m^2 - 1,2 m^3,$$

$m = 0,5$ molar eritmaning parsial mol hajmini aniqlang.

Y e c h i s h . (VI.3) tenglamaga muvofiq:

$$V_{\text{NaCl}} = \left(\frac{\partial V_{um}}{\partial n_{\text{NaCl}}} \right)_{T, P, j} = \frac{\partial (55,55 \cdot V_{\text{H}_2\text{O}} + 16,4 \cdot m + 2,5 \cdot m^2 - 1,2 \cdot m^3)}{\partial m} =$$

$$= 16,4 + 5m - 3,6m^2 = 18,0.$$

2. Tarkibi bo'yicha 40% etanol $\text{C}_2\text{H}_5\text{OH}$ tutgan eritmaga 100 gramm etanol qo'shilganda eritma hajmi qanchaga o'zgaradi? 1 mol suv qo'shilganda eritma hajmi $0,4 \text{ sm}^3/\text{mol}$ ga o'zgaradi. Eritma zichligi $d_1 = 0,936 \text{ g/sm}^3$, suvning zichligi $d_{\text{H}_2\text{O}} = 1,000 \text{ g/sm}^3$, etanol zichligi $d_2 = 0,87 \text{ g/sm}^3$.

Yechish. Agar V_1 oldingi va V_2 oxirgi hajm bo'lsa,

$$V_2 = V_1 + n_2 \Delta \bar{V}_2 = V_1 + \frac{100}{M_2} \Delta \bar{V}_2$$

$$\Delta V = V_2 - V_1 = \frac{100}{M_2} \Delta \bar{V}_2,$$

M_2 — spirtning molekular massasi.

(VI.7) tenglamaga muvofiq:

$$\Delta \bar{V}_2 = \bar{V}_2 - V_2^0 \quad \text{va} \quad \Delta \bar{V}_2 = \frac{100}{M_2} (\bar{V}_2 - V_2^0) = \frac{100}{M_2} \bar{V}_2 - \frac{100}{d_2} \dots\dots(a).$$

Demak, masalani yechishda ΔV qiymatini aniqlash uchun $\bar{V}_2$ ning qiymatini topish kerak. $\bar{V}_2$ ning qiymati (VI.3) tenglamadan foydalanib aniqlanadi:

$$V_{um} = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

$$V_{um} = \frac{100}{d_1}; \quad n_1 = \frac{g_1}{M_1}; \quad n_2 = \frac{g_2}{M_2}; \quad \bar{V}_1 = V_1^0 + \Delta V_1 \quad (\text{VI.12})$$

tenglamadan

$$V_1^0 = \frac{M_1}{d_1}.$$

Bu qiymatlar yuqoridagi tenglamaga qo'yilsa:

$$\frac{100}{d_1} = \frac{g_1}{M_1} \left(\frac{M_1}{d_1} + \Delta \bar{V}_1 \right) + \frac{g_2}{M_2} \bar{V}_2,$$

bundan,

$$\bar{V}_2 = \frac{100 \cdot M_2}{d_1 \cdot g_2} - \frac{M_2 \cdot g_1}{d_1 \cdot g_2} - \frac{M_2 \cdot g_1}{M_1 \cdot g_2} \cdot \Delta \bar{V}_1 \dots (b).$$

(b) ning qiymati (a) tenglamaga qo'yilsa:

$$\Delta V = \frac{104}{d_1 g_2} - \frac{100 g_1}{d_1 \cdot g_2} - \frac{100 \cdot g_1}{M_1 \cdot g_2} \Delta \bar{V}_1 - \frac{100}{d_2},$$

ya'ni

$$\Delta V = \frac{104}{0,930 \cdot 40} - \frac{100 \cdot 60}{1 \cdot 40} - \frac{100 \cdot 60}{18 \cdot 40} (-0,4) - \left(\frac{100}{0,87} \right) =$$

$$= 257 - 150 + 3 - 115 = -5 \text{ sm}^3.$$

3. 298,2 K da grafik usul bilan 60% li metanol eritmasida suv va metanolning parsial mol hajmini aniqlang. Masalani yechishda metanol eritmasi zichligining cruvchi konsentratsiyasi o'zgarishining bog'liqligidan foydalaning:

spirt, %	0	20	40	60	80	90	100
d, g/sm ³	0,9982	0,9666	0,9345	0,8946	0,8400	0,8202	0,7917

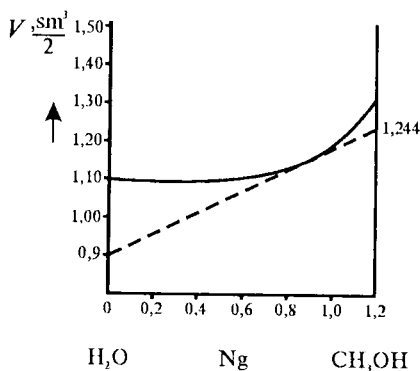
Y e c h i s h . Massa bilan ifodalangan foiz konsentratsiyani massa nisbatiga $N_{g_i} = \frac{g_i}{\sum g_i}$, zichlikni esa solishtirma hajmga $(V = \frac{g_i}{\sum g_i})$ aylantiramiz:

CH ₃ OH, %	0	20	40	60	80	90	100
gCH ₃ OH	0	0,2	0,4	0,6	0,8	1,9	1,0
V, sm ³ /g	1,002	1,035	1,070	1,118	1,181	1,219	1,263

Bu qiymatlar V—Ng koordinataga qo'yiladi (VI.2-rasm). 60% konsentratsiyaga to'g'ri kelgan nuqtadan urinma o'tkazib, ordinata chiziqlari bilan kesishguncha davom ettiriladi. Rasmdan $\bar{V}_{\text{CH}_3\text{OH}} = 1,244 \text{ sm}^3/\text{g}$, $\bar{V}_{\text{H}_2\text{O}} = 0,931$ topiladi. Parsial mol hajm $\bar{V}_i = V_i \cdot M_i$ dan aniqlanadi. Demak,

$$\bar{V}_{\text{CH}_3\text{OH}} = 1,244 \cdot 3,2 = 29,8 \text{ sm}^3/\text{g},$$

$$\bar{V}_{\text{H}_2\text{O}} = 0,931 \cdot 18 = 16,78 \text{ sm}^3/\text{g}.$$



VI.2-rasm. H_2O va CH_3OH ning
parsial mol hajmini aniqlash.

4. Talliy (2) — simob (1)
eritmasida talliyning molar qis-
mi $N_2 = 0,45$ ga teng. 298 K da
parsial izobarik potensial va
parsial entropiyaning o'zgarishi
 $\Delta \bar{G}_2 = -163,3 \text{ J/mol}$,
 $\Delta \bar{G}_1 = -2130 \text{ J/mol}$,
 $\Delta \bar{S}_2 = 3,48 \text{ J/mol} \cdot \text{grad}$,
 $\Delta \bar{S}_1 = 5,4 \text{ J/mol} \cdot \text{grad}$ ga teng.

Shu konsentratsiyadagi eritma
toza komponentlardan 1 kg
tayyorlanganda parsial entalpiyaning o'zgarishi, entalpiya, entropiya
va izobarik potentsiallarning o'zgarishi qanchaga teng bo'ladi?

Yechish. (VI.11) tenglamadan foydalanib, 1 mol eritma
uchun izobar potentsialning o'zgarishini aniqlaymiz:

$$\begin{aligned}\Delta G &= N_1 \Delta \bar{G}_1 + N_2 \Delta \bar{G}_2 = \\ &= 0,55(-2130) + 0,45(-163,3) = \\ &= -1215 \text{ J/mol}.\end{aligned}$$

1 mol eritmaning massasi

$$\begin{aligned}g &= n_1 M_1 + n_2 M_2 = 0,55 \cdot 200,6 + \\ &+ 0,45 \cdot 204,4 = 202,3 \text{ g}.\end{aligned}$$

1 kg eritmadagi izobar potentsialning o'zgarishini hisoblaymiz:

$$\Delta G = -1245 \frac{1000}{202,3} = -6150 \text{ J/kg}.$$

1 mol eritma uchun entropiyaning o'zgarishini aniqlaymiz:

$$\Delta S = N_1 \Delta \bar{S}_1 + N_2 \Delta \bar{S}_2 = 0,55 \cdot 5,4 + 0,45 \cdot 3,48 = 4,54 \text{ J/mol} \cdot \text{grad}.$$

Entropiya o'zgarishini 1 kg eritma uchun hisoblaymiz:

$$\Delta S = 4,54 \frac{1000}{202,3} = 22,4 \text{ J/kg} \cdot \text{grad}.$$

1 kg eritma uchun entalpiyaning o'zgarishini hisoblaymiz:

$$\Delta H = \Delta G + T\Delta S = -6150 + 298 \cdot 22,4 = -534 \text{ J/kg.}$$

Ikkala komponent uchun parsial mol entalpiyaning o'zgarishini aniqlaymiz:

$$\Delta \bar{H}_1 = \Delta \bar{G}_1 + T\Delta \bar{S}_1 = -2130 + 298 \cdot 5,4 = -521 \text{ J/mol.}$$

$$\Delta \bar{H}_2 = \Delta \bar{G}_2 + T\Delta \bar{S}_2 = -1630 + 298 \cdot 3,48 = 874 \text{ J/mol.}$$

VI.3. ERISH ISSIQLIK EFFEKTI

Gaz, suyuq va qattiq holdagi moddalar sof erituvchida yoki birorta eritmada eriganda issiqlik ajralib chiqadi yoki issiqlik yutiladi. Bu issiqlik **erish issiqlik effekti** (ΔH_{erish}) deyiladi. Erish issiqlik effektini sxema tarzida ikki issiqlikning yig'indisi deb tasavvur qilish mumkin, ya'ni:

$$\Delta H_{erish} = \Delta H_1 + \Delta H_2, \quad (\text{VI.13})$$

bunda: ΔH_1 — qattiq holdagi moddalar kristall panjaralarining buzilishi uchun sarflangan (yutilgan) issiqlik; ΔH_2 — cruvchi va erituvchi moddalarning o'zaro ta'sirlanishi natijasida ajralgan issiqlik.

Ko'pincha $\Delta H_1 > \Delta H_2$ bo'ladi va shu sababdan qattiq moddalarning erishida issiqlik aksariyat holatlarda yutiladi va bu sharoitda eritma soviydi.

Gazlar eriganda ΔH_1 — gaz torayib erituvchi hajmini qabul qilishi natijasida ajralgan issiqlik, ΔH_2 — gaz va erituvchi o'zaro ta'sirlashganda ajralib chiqqan issiqlik. Shunga ko'ra, gazlar erituvchi yoki eritmalarda eriganda issiqlik ajralib chiqib, eritma isiydi.

Erish issiqlik effekti ifodalari. 1 mol modda n mol toza erituvchida erib, m konsentratsiyali eritma hosil qilganda ajralib

chiqqan (yoki yutilgan) issiqlik *integral erish issiqlik effekti* (ΔH_m) deyiladi.

Ma'lum konsentratsiyadagi eritmaga eruvchi modda qo'shib eritma konsentratsiyasi oshirilganda yoki erituvchi qo'shilib eritma suyultirilganda issiqlik ajraladi (yoki yutiladi). 1 mol eruvchi modda juda katta hajmdagi ma'lum konsentratsiyaga ega bo'lgan eritmaga qo'shilgan holatda ajralgan yoki yutilgan issiqlikni konsentrlash *parsial* yoki *differensial erish issiqlik effekti* (ΔH_D) deyiladi. Eritma m_1 dan m_2 konsentratsiyaga o'zgarganda ($m_2 > m_1$):

$$\Delta H_D = \Delta H_{m_1} - \Delta H_{m_2} \text{ ga teng.} \quad (\text{VI.14})$$

ΔH_{m_1} , ΔH_{m_2} lar m_1 , m_2 konsentratsiyali eritmaning integral issiqlik effekti.

Ma'lum konsentratsiyadagi eritmaga erituvchi qo'shib eritmani suyultirishda ham issiqlik effekti namoyon bo'ladi. Bu *suyultirish issiqlik effekti* deb ataladi. 1 mol eruvchi modda tutgan m_1 konsentratsiyali eritmaga erituvchi qo'shib eritma cheksiz suyultirilgandagi issiqlik effekti *integral suyultirish issiqlik effekti* ($\Delta H_{m_1}^0$) deyiladi:

$$\Delta H_{m_1}^0 = \Delta H_0 - \Delta H_{m_1}, \quad (\text{VI.15})$$

ΔH_0 — 1 mol eruvchi modda cheksiz katta hajmdagi erituvchida erigan sharoitdagi issiqlik effekti, ΔH_{m_1} — m_1 konsentratsiyali eritma hosil bo'lgandagi issiqlik effekti.

Ma'lum konsentratsiyadagi eritmaga 1 mol erituvchi qo'shib eritma suyultirilgandagi issiqlik effekti *parsial* yoki *differensial suyultirish issiqlik effekti* (ΔH_c) deb ataladi, ya'ni:

$$\Delta H_c = \Delta H_{m_1} - \Delta H_{m_2}. \quad (\text{VI.16})$$

Umuman,

$$\Delta H_D = \left(\frac{\partial \Delta H_m}{\partial n_2} \right)_{T, P, n_1}. \quad (\text{VI.17})$$

Agar ΔH_q bo'lsa, ΔH_D Δm o'rnida Δm_2 , agar ΔH_s bo'lsa, Δm_1 qo'yiladi.

Bunda n_2 — eruvchining, n_1 — erituvchining mol soni.

Integral va differensial erish issiqliklari eritma konsentratsiyasi, harorat, erigan modda va erituvchi xossalriga bog'liq holda o'zgaradi.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Massasi 2 g bo'lgan KCl 100 g suvda 298 K da erib, eritma hosil qilgan. Kaliy xloridning erish issiqligi topilgan. KCl ning mol massasi $M_{\text{KCl}} = 74,5$ ga teng.

Yechish. KCl eritmasining molal (m) konsentratsiyasini aniqlaymiz:

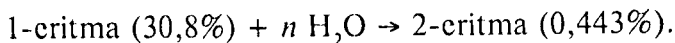
$$\begin{aligned} 2/74,5 &= 100 \text{ gH}_2\text{O} \\ m &= 1000 \text{ gH}_2\text{O} \\ m &= \frac{2 \cdot 10}{74,5} = 0,269 \text{ mol} / 1000 \text{ g.} \end{aligned}$$

Ma'lumotnomadan KCl ning suvda 298 K da erishining integral issiqligini topamiz. $\Delta H_m = 17,56 \cdot 10^3 \text{ kJ/mol}$. Shunga ko'ra, 2 g KCl ning erish issiqligi quyidagicha hisoblanadi:

$$\begin{aligned} 1 \text{ mol KCl} &= \Delta H_{m,1} \\ 0,269 \text{ KCl} &= \Delta H_{m,2} \\ \Delta H_{m,2} &= 0,269 \cdot 17,56 \cdot 10^3 = 4710 \text{ J} = 4,71 \text{ kJ.} \end{aligned}$$

2. NaOH eritmasi 30,8 % dan 0,443% gacha suyultirilgan. Standart differensial erish issiqlik (ΔH) effektini aniqlang.

Yechish. Ma'lumotnomalarda konsentratsiyasi 1 mol NaOH ga n mol H_2O to'g'ri kelishi bilan ifodalangan suyultirish jarayonini sxema tarzida quyidagicha ifoda qilish mumkin:



Demak:

$$\Delta H_c = \Delta H_{m,2} (2\text{-eritma}) - \Delta H_{m,1} (1\text{-eritma})$$

va

1- va 2-eritmalarida 2NaOH n mol suvga to'g'ri kelganligini aniqlab, so'ng $1:n$ nisbatga to'g'ri kelgan integral erish issiqliklarini yuqoridagi tenglamaga qo'yish kerak bo'ladi.

$M_{\text{NaOH}} = 23 + 16 + 1 = 40$. Shuning uchun eritma konsentratsiyasi % bilan ifodalangan $1:n$ ifodasiga aylantiriladi:

$$\frac{30,8}{40,0} \text{ mol NaOH} \quad \frac{69,2}{18,0} \text{ mol suvda erigan}$$

1 mol NaOH — x mol suvda erigan.

$$x_1 = \frac{69,2 \cdot 40,0}{18,0 \cdot 30,8} = 5.$$

5 mol suv 1 mol NaOH ga to'g'ri keladi ($1:n = 1:5$).

Xuddi shunday:

$$\frac{0,443}{40,0} \text{ mol NaOH} \quad \frac{99,558}{18,0} \text{ suvda erigan.}$$

$$x_2 = \frac{99,558 \cdot 40,0}{18,0 \cdot 0,443} = 500,$$

demak, shuncha mol suv 1 mol NaOH ga to'g'ri keladi.

Integral standart erish issiqlik effekti ma'lumotnomadan olinadi.

$$n_{\text{NaOH}} : n_{\text{H}_2\text{O}} = 1:5 \text{ bo'lganda } \Delta H_m = - 37,76 \text{ kJ.}$$

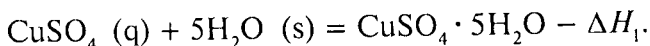
Bu nisbat $\text{NaOH} : \text{H}_2\text{O} = 1:500$ bo'lganda $\Delta H_m = - 42,36 \text{ kJ}$.

Demak: $\Delta H_c = - 42,36 - (-37,76) = - 4,6 \text{ kJ/mol}$.

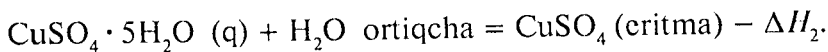
Masala yechimiga ko'ra suyultirish issiqlik ajralishi bilan boradi.

3. Mis sulfat (CuSO_4) va suvning (H_2O) oddiy moddalardan standart hosil bo'lish issiqlik effektlari mos ravishda — 771 va — 286 kJ/mol ga teng. Gidratlangan mis sulfatning $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ suvda integral erish issiqligi 11,7 kJ/mol ga teng. 1 mol suvsiz mis sulfat CuSO_4 ning suvda erish issiqligi qanchaga teng?

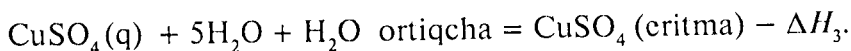
Yechish. Faraz qilaylik, CuSO_4 ning erishi ikki bosqich bilan boradi. Suvsiz tuzning suvlanishi:



Suvlangan tuzning juda katta miqdordagi ortiqcha suvda erishi:



Agar bu ikki tenglama qo'shilsa, issiqlik effektini aniqlash kerak bo'lgan reaksiya kelib chiqadi:



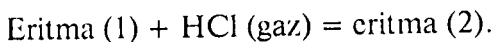
Demak:

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

va Gess qonuniga muvofiq: $\Delta H_1 = \Delta H(\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \text{ ning hosil bo'lishi}) - \Delta H(\text{CuSO}_4 \text{ ning hosil bo'lishi}) + 5 \Delta H (\text{suvning hosil bo'lishi})$. Unda $\Delta H_3 = -2280 - (-771 - 5 \cdot 286) + 11,7 = -67 \text{ J}$.

4. 298 K va $1,013 \cdot 10^5 \text{ Pa}$ bosimda 3 kg 10% HCl eritmasida gazsimon 0,1 kg HCl eritilgan. Erish (konsentrlash) issiqlik effektini aniqlang.

Yechish. Erish jarayonini sxematik ravishda quyidagicha tasvirlash mumkin:



(VI.16) tenglamaga muvofiq:

$$\Delta H_c = \Delta H_{m_2} - \Delta H_{m_1},$$

ΔH_{m_1} — (1) eritma hosil bo'lish jarayonidagi issiqlik effekti, ΔH_{m_2} — (2) eritma hosil bo'lish jarayonidagi issiqlik effekti. Yuqoridagi tenglama 1 mol eritma uchun to'g'ri ($n = 1$). Ergan n modda uchun ΔH_{m_1} va ΔH_{m_2} larni erigan moddalarning mol soniga ko'paytirish kerak:

$$\Delta H_c = (n_1 + n_2)\Delta H_{m_2} - n_1\Delta H_{m_1},$$

n_1 — eritma (1) dagi HCl ning mol soni, n_2 — 10% li eritmada erigan HCl ning mol soni.

n_1, n_2 va suv mollari aniqlanadi (kg dan grammga o'tiladi):

$$n_{\text{H}_2\text{O}} = \frac{3000 \cdot 0,9}{18} = 150; \quad n_1 = \frac{3000 \cdot 0,1}{36,5} = 8,219, \quad n_2 = \frac{100}{36,5} = 2,739.$$

Bu miqdorlarning molar qismi ifodasiga o'tkaziladi:

$$\frac{n_{\text{H}_2\text{O}}}{n_1} = \frac{150}{8,219} = 18,26; \quad \frac{n_{\text{H}_2\text{O}}}{n_1 + n_2} = \frac{150}{8,219 + 2,739} = 13,69.$$

Ma'lumotnomadan integral erish issiqligi topiladi:

$$\Delta H_{m_1} = -71,6; \quad \Delta H_{m_2} = 70,6 \text{ kJ/mol}.$$

Bu ma'lumotlar yuqoridagi tenglamaga qo'yilsa:

$$\Delta H_{\bar{n}} = (n_1 + n_2) \Delta H_{m_2} - n_1 \Delta H_{m_1} = [(8,219 + 2,739) \cdot (-70,6)] - [8,219 \cdot (-71,6)] = -185,2 \text{ kJ}.$$

SUYULTIRILGAN ERITMALAR XOSSASI

VI.4. RAUL QONUNI

Agar bir-birida cheksiz erigan suyuqlikdan iborat eritma va P_1^0, P_2^0 — moddalarning toza holdagi to'yingan bug' bosimi hamda P_1, P_2 — shu haroratdagi mana shu moddalarning eritma ustidagi to'yingan bug' bosimi bo'lsa, u holda doimo $P_1^0 > P_1$ bo'ladi.

Bunda $\Delta P_1 = P_1^0 - P_1$ yoki $\Delta P_2 = P_2^0 - P_2$ — **bug' bosimining kamayishi** va $\frac{P_1^0 - P_1}{P_1^0}$ — **bug' bosimining nisbiy kamayishi** deyiladi.

Raul qonuniga muvofiq birinchi modda bug' bosimining nisbiy kamayishi eritmadagi ikkinchi moddaning molar qismiga teng, ya'ni:

$$\frac{P_1^0 - P_1}{P_1^0} = N_2 \quad \text{va} \quad \frac{P_2^0 - P_2}{P_2^0} = N_1. \quad (\text{VI.18})$$

Agar $N_1 + N_2 = 1$ ga teng ekanligini hisobga olsak,

va

$$1 - \frac{P_1}{P_1^0} = 1 - N_1$$

$$P_1 = N_1 P_1^0 \text{ hamda } P_2 = N_2 P_2^0. \quad (\text{VI.19})$$

(VI.18) va (VI.19) tenglamalar Raul qonunining matematik ifodasi bo'lib, bu qonunga bo'ysungan eritmalar **ideal eritmalar** deb ataladi.

Eritmaning umumiy bosimi P ga teng:

$$P = N_1 P_1^0 + N_2 P_2^0 = P_2^0 + N_1 (P_1^0 - P_2^0). \quad (\text{VI.20})$$

Agar erituvchi modda uchuvchan bo'lmasa (ya'ni qattiq modda bo'lsa), u holda eritmaning bug' bosimi erituvchining eritma ustidagi bug' bosimi P_1 ga teng bo'ladi.

Eritmalar o'ta suyultirilgan bo'lsa, erituvchining mol sonining (n_2) erituvchining mol soniga (n_1) nisbati hisobga olinmasa ham bo'ladi, ya'ni $n_1 + n_2 \cong n_1$ deb qabul qilinadi. Shunga ko'ra:

$$\frac{P_1^0 - P}{P_1^0} = \frac{\Delta P}{P_1^0} = N_2 = \frac{n_2}{n_1 + n_2} \cong \frac{n_2}{n_1}, \quad (\text{VI.21})$$

bunda

$$n_1 = \frac{g_1}{M_1}; \quad n_2 = \frac{g_2}{M_2},$$

bunda: g_1 — erituvchi miqdori (g, kg);

g_2 — erigan modda miqdori (g, kg).

Eritmada erigan moddaning molekular massasi quyidagi tenglama bo'yicha aniqlanadi:

$$M_2 = \frac{g_2 M_1}{g_1} \cdot \frac{P_1^0}{\Delta P}. \quad (\text{VI.22})$$

MASALALAR YECHISHIGA DOIR MISOLLAR

1. 100°C da 5% li shakar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) eritmasining bug' bosimi va suvli eritmadagi glitserin miqdorini foizda hisoblang. Bunda glitserinning suvli eritmasi bug' bosimi 5% li shakar eritmasi bug' bosimiga teng hamda 5% li shakar eritmasi o'ta suyultirilgan eritmalar qonuniga bo'ysunadi, deb hisoblansin. Glitserin $\text{C}_3\text{H}_8\text{O}_3$

ning mol massasi $M_2 = 92,09$ ga teng. Shakarning mol massasi $M_1 = 342$.

Yechish. 1) 5% li shakar critmasining bug' bosimini yuqoridagi tenglamalar asosida hisoblaymiz:

$$P_1 = N_1 P_1^0 = P_1^0 (1 - N_2) \text{ va } P_1 = P_1^0 - P_1^0 N_2,$$

bunda: $P_1^0 = 760$ mm sim. ust.,

$$P_{\text{H}_2\text{O}} = 760 - 0,0028 \cdot 760 = 757,87 \text{ mm. sim. ust.}$$

Shakarning suvdagi molar qismi quyidagicha aniqlanadi:

$$N_2 = \frac{\frac{g_2}{M_2}}{\frac{g_2}{M_2} + \frac{g_1}{M_1}} = \frac{\frac{5}{342,3}}{\frac{5}{342,3} + \frac{95}{18,0}} = 0,0028.$$

Suvli critmadagi glitserinning foiz miqdorini aniqlaymiz. Masala shartiga ko'ra, glitserin critmasi bug' bosimi shakar critmasi bug' bosimiga teng, shu sababli glitserinning molar qismi 0,0028 ga teng. Glitserinning konsentratsiyasi:

$$g_2 = \frac{100 \cdot N_2 \cdot M_2}{N_2 M_2 + N_1 M_1} = \frac{100 \cdot 0,0028 \cdot 92,09}{0,0028 \cdot 92,09 + 0,9972 \cdot 18} = 1,42\%.$$

2. Metil xlorid ustidagi to'yingan bug' bosimi 273 K da $P_{\text{CH}_3\text{Cl}}^0 = 2,64 \cdot 10^5$ Pa, etil xlorid critmasi ustidagi bug' bosimi esa $P_{\text{C}_2\text{H}_5\text{Cl}}^0 = 0,638 \cdot 10^5$ Pa ga teng. Etil xloridning metil xloriddagi critmasi Raul qonuniga bo'ysunadi deb qabul qilinib, 50% li critmadagi bug' tarkibi (molar qismi) aniqlansin.

Yechish. Masala shartida moddalarning to'yingan bug' bosimi berilgan. Bug' bosimlaridan critmaning bug'dagi tarkibiy qismi mol soniga o'tish uchun Daltonning parsial bug' bosimi qonunidan foydalaniladi:

$$\frac{n_1}{n_2} = \frac{P_1}{P_2},$$

bunda: n_1, n_2 — moddalarning bug'dagi mol soni.

Demak, avvalo parsial bug' bosimlarini aniqlash kerak. Bug'ning tarkibini aniqlash uchun metil xlorid va etil xloridning parsial bosimlari Raul qonuni tenglamasidan foydalanib hisoblanadi.

Masala shartiga ko'ra, eritma tarkibi foiz miqdorida berilganligi sababli, oldin uni mol miqdorga va so'ngra molar qismga aylantirish kerak:

$$M_{\text{CH}_3\text{Cl}} = 50,5; \quad M_{\text{C}_2\text{H}_5\text{Cl}} = 64,5.$$

100 g eritmada mol miqdorlar teng:

$$n_{\text{CH}_3\text{Cl}} = \frac{50}{50,5} = 0,99,$$

$$n_{\text{C}_2\text{H}_5\text{Cl}} = \frac{50}{64,5} = 0,775.$$

Eritmadagi molar qismni hisoblaymiz:

$$N_{\text{CH}_3\text{Cl}} = \frac{0,99}{0,99+0,775} = 0,561,$$

$$N_{\text{C}_2\text{H}_5\text{Cl}} = \frac{0,775}{0,99+0,775} = 0,439.$$

Parsial bug' bosimlarini aniqlaymiz:

$$P_{\text{CH}_3\text{Cl}} = P_{\text{CH}_3\text{Cl}}^0 \cdot N_{\text{CH}_3\text{Cl}} = 2,64 \cdot 10^5 \cdot 0,561 = 1,48 \cdot 10^5 \text{ Pa},$$

$$P_{\text{C}_2\text{H}_5\text{Cl}} = P_{\text{C}_2\text{H}_5\text{Cl}}^0 \cdot N_{\text{C}_2\text{H}_5\text{Cl}} = 0,638 \cdot 10^5 \cdot 0,433 = 0,28 \cdot 10^5 \text{ Pa}.$$

Endi bug'ning tarkibini molar qismda topamiz. Daltonning parsial bosimlar qonuniga muvofiq:

$$\frac{n_1}{n_2} = \frac{P_1}{P_2}.$$

$$\text{Demak, } N_{\text{bug}', \text{CH}_3\text{Cl}} = \frac{P_{\text{CH}_3\text{Cl}}}{P_{\text{CH}_3\text{Cl}} + P_{\text{C}_2\text{H}_5\text{Cl}}} = \frac{1,48}{1,48+0,28} = 0,841,$$

$$N_{\text{bug}', \text{C}_2\text{H}_5\text{Cl}} = \frac{P_{\text{C}_2\text{H}_5\text{Cl}}}{P_{\text{CH}_3\text{Cl}} + P_{\text{C}_2\text{H}_5\text{Cl}}} = \frac{0,28}{1,76} = 0,159.$$

3. Uchuvchan bo'lmagan (qattiq modda) eruvchi modda tutgan suvli eritmaning bug' bosimi toza erituvchi (suv)ning bug' bosimidan 2% kam. Eritmaning molal konsentratsiyasi (m)ni aniqlang.

Y e c h i s h . (VI.18) tenglamadan foydalanamiz. Agar suvning bug' bosimi 100 mm simob ustuniga teng deb faraz qilinsa, masala shartiga muvofiq eritma bug' bosimi 2% ga kam, ya'ni 98 mm sim. ust.ga teng bo'ladi:

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{100 - 98}{100} = N_2; \quad N_2 = 0,2.$$

Molar qismdan eruvchi moddalarning mol soni (n) aniqlanadi:

$$N_2 = \frac{n_2}{n_1 + n_2},$$

$$n_1 - \text{suvning mol soni: } n_1 = \frac{1000}{18} = 55,56.$$

$$N_2 = \frac{n_2}{n_1 + n_2}; \quad 0,02 = \frac{n_2}{55,56 + n_2}.$$

Bu tenglamadan: $n_2 = m = 1,134$ mol.

Demak, 1000 g suvda 1,134 mol eruvchi modda erigan, ya'ni:

$$m = 1,134.$$

VI.5. ERITMALARNING MUZLASH HARORATI

Eritma doimo toza erituvchiga nisbatan past haroratda muzlaydi. Eritmalar muzlash haroratining pasayishi — ΔT shu eritmada erigan modda konsentratsiyasiga (m) to'g'ri mutanosib (proporsional)dir, ya'ni:

$$\Delta T = K \cdot m. \quad (\text{VI.23})$$

Dissotsilanadigan modda uchun:

$$\Delta T = i K m, \quad (\text{VI.24})$$

bunda i — izotonik koeffitsiyent $\Delta T = T_0 - T$ ga teng.

Bunda: T_0 — toza erituvchining muzlash harorati;

T — eritmaning muzlash harorati;

m — erigan moddaning molal konsentratsiyasi;

K — proporsionallik koeffitsiyenti yoki *krioskopik doimiylik* deb ataladi.

Agar $m = 1$ bo'lsa, $K = \Delta T_m$ bo'ladi. Demak, K — 1 molal eritma muzlash haroratining pasayishiga teng. K faqat erituvchining tabiati va xossasiga bog'liq bo'lib, eriyotgan modda tabiatiga bog'liq emas. Har bir erituvchining K si o'ziga xos qiymatga ega. Turli erituvchilar uchun K ning qiymati ma'lumotnomalarda berilgan.

Krioskopik konstanta (doimiylik) quyidagicha hisoblanadi:

$$K = \frac{R \cdot (T_0)^2 \cdot M_1}{1000 \cdot \Delta H}, \quad (\text{VI.25})$$

bunda: M_1 — erituvchining mol massasi; T_0 — erituvchining muzlash harorati; ΔH — toza erituvchining suyuqlanish issiqlik effekti (J/mol); R — universal gaz doimiysi.

Agar G g erituvchida gramm modda erigan bo'lsa, molal konsentratsiya (m) quyidagicha bo'ladi:

$$m = \frac{g \cdot 1000}{M_2 \cdot G}, \quad (\text{VI.26})$$

M_2 — erituvchining molekular massasi.

(VI.26) tenglamani (VI.23) tenglamaga qo'ysak:

$$\Delta T = \frac{K \cdot g \cdot 1000}{M_2 \cdot G}. \quad (\text{VI.27})$$

Shunga ko'ra, (VI.27) tenglamadan:

$$M_2 = \frac{K \cdot g \cdot 1000}{\Delta T \cdot G}. \quad (\text{VI.28})$$

Demak, cheksiz suyultirilgan eritmalarda erigan moddaning molekular massasi (VI.28) tenglama asosida aniqlanadi. Shu sababli

moddalarining molekular massasini eritma muzlash haroratining pasayishi orqali aniqlash usuliga **krioskopik usul** deyiladi.

MASALALAR YECHISHGA DOIR MISOLLAR

1. Muzlash harorati 315 K, krioskopik doimiysi 5,2 bo'lgan n toluidin ($\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) ning suyuqlanish issiqligini aniqlang.
 Yechish. (6.25) tenglamadan foydalanib ΔH_{suyuq} ni topamiz:

$$\Delta H_{\text{suyuq}} = \frac{R(T_0)^2}{1000 \cdot K} = \frac{8,31 \cdot 10^3 \cdot 315^2}{1000 \cdot 5,2} = 1,59 \cdot 10^5 \text{ (J/kg)}.$$

2. Texnik sirka kislota 16,4°C da muzlaydi. Toza holdagi sirka kislota esa 16,7°C da muzlaydi va uning krioskopik doimiysi 3,9 ga teng. Texnik sirka kislota dagi qo'shimchalarning molal konsentratsiyasini hisoblang.

Yechish. Sirka kislota ning qo'shimchalar ishtirokidagi muzlash harorati pasayishini aniqlaymiz:

$$\Delta T_m = T^0 - T_m = 16,7 - 16,4 = 0,3^\circ.$$

(VI.31) tenglamaga muvofiq 1000 g dagi sirka kislota qo'shimchalari miqdorini, ya'ni konsentratsiyasini hisoblaymiz:

$$m = \frac{\Delta T}{K} = \frac{0,3}{3,9} = 0,08 \text{ mol}.$$

3. Tarkibida 100 g benzol va 0,2 g tekshirilayotgan moddasi bor eritmaning muzlash harorati toza benzolning muzlash haroratiga nisbatan 0,17 K ga past. Krioskopik konstantasi 5,16 grad/mol ga teng. Moddaning molekular massasini hisoblang.

Yechish. Eritmada erigan moddaning molekular massasini (VI.28) tenglamadan foydalanib topamiz:

$$M = \frac{1000 \cdot 5,16 \cdot 0,2}{100 \cdot 0,17} = 60,23.$$

4. Kamforaning krioskopik doimiysi 40 ga, suyuqlanish harorati 452 K ga teng. Tarkibida 1% mochevina — $(\text{NH}_2)_2\text{CO}$ bo'lgan

kamfora aralashmasining suyuqlanish haroratini toping. Mochevinaning molekular massasi $M_m = 60$.

Yechish. (VI.24) tenglamaga muvofiq $\Delta T = T_0 - T$ va $T = T_0 - \Delta T$. Demak, masalani yechish uchun avval ΔT aniqlanishi kerak. Bu (VI.27) tenglamadan topiladi.

Masala sharti bo'yicha eritma $g = 1$ g mochevina va $G = 99$ g kamforadan iborat.

(VI.27) tenglamaga muvofiq:

$$\Delta T = \frac{K \cdot g \cdot 1000}{G \cdot M_2} = \frac{40 \cdot 1 \cdot 1000}{99 \cdot 60} = 6,75.$$

$\Delta T = T_0 - T$ (T_0 —erituvchi, T —eritmaning muzlash harorati) bo'lganligidan:

$$T = T_0 - \Delta T = 452 - 6,75 = 445,25 \text{ K}.$$

VI.6. ERITMALARNING QAYNASH HARORATI

Eritmaning qaynash harorati eritma konsentratsiyasi ortgan sari ko'tarilib boradi va cheksiz suyultirilgan elektrolit bo'lmagan eritmalar uchun bu holat quyidagicha ifodalanadi:

$$\Delta T_q = E \cdot m. \quad (\text{VI.29})$$

Dissotsialanuvchi modda uchun $\Delta T_q = iEm$.

Bunda: $\Delta T_q = T - T_0$ — qaynash haroratining ko'tarilishi;

T_0, T — erituvchi va eritmaning qaynash harorati;

ΔT — eritma qaynash haroratining ko'tarilishi;

E — proporsionallik koeffitsiyenti yoki ebulioskopik konstanta (doimiysi).

Ebulioskopik konstanta quyidagicha ifodalanadi:

$$E = \frac{R \cdot (T_0)^2 \cdot M_1}{1000 \cdot \Delta H}, \quad (\text{VI.30})$$

bunda: T_0 — toza erituvchining qaynash harorati, K;

ΔH — toza erituvchining molar bug‘lanish issiqligi (J/mol).

Erigan moddaning molekular massasi quyidagi tenglama asosida hisoblanadi:

$$M_2 = \frac{E \cdot g \cdot 1000}{\Delta T \cdot G}. \quad (\text{VI.31})$$

MASALALAR YECHISHGA DOIR MISOLLAR

1. 373 K da bug‘lanish issiqligi $2,464 \cdot 10^3$ J/mol bo‘lgan suvning ebullioskopik konstantasini aniqlang.

Yechish. (VI.30) tenglamadan foydalanib, E ni hisoblaymiz:

$$E = \frac{8,314 \cdot 373,16^2}{1000 \cdot 2,464 \cdot 10^3} = 0,513 \text{ kJ/mol}$$

2. Elektrolit bo‘lmagan 0,6 g modda 25 g suvda eriganda eritmaning qaynash harorati $0,204^\circ\text{C}$ ga ko‘tariladi. Shu moddaning 0,3 g i 20 g benzolda eriganda esa eritmaning qaynash harorati $0,668^\circ\text{C}$ ga ortadi. Suvning ebullioskopik doimiysi 0,512. Benzolning ebullioskopik doimiysini toping.

Yechish. (VI.30) tenglama bo‘yicha $E = \frac{M_2 \cdot G \cdot \Delta T}{1000 \cdot g}$, bunda M_2 ni aniqlash kerak. Uni suvli eritma ma’lumotlaridan foydalanib topish mumkin.

(VI.31) tenglamaga binoan suvda erigan moddaning molekular massasi:

$$M_2 = \frac{E_{\text{H}_2\text{O}} \cdot g \cdot 1000}{\Delta T_q \cdot G} = \frac{0,512 \cdot 0,6 \cdot 1000}{0,204 \cdot 25} = 60.$$

Shu tenglamadan foydalanib benzolning ebullioskopik doimiysini topamiz:

$$E_{\text{C}_6\text{H}_6} = \frac{\Delta T_q \cdot M_2 \cdot G}{g \cdot 1000} = \frac{0,668 \cdot 60 \cdot 20}{0,3 \cdot 1000} = 2,67.$$

3. Suvning bug‘lanish issiqligi $\Delta H_{\text{bug}} = 40,685$ kJ/mol ga teng. Uning ebullioskopik konstantasini toping.

Yechish. Suvning ebulioskopik konstantasini (VI.30) tenglamadan foydalanib hisoblaymiz:

$$E = \frac{8,314 \cdot 373,16^2 \cdot 18}{1000 \cdot 40,685} = 0,512 \text{ grad/mol.}$$

4. Harorat 458 K da anilinning bug‘lanish issiqlik effektini hisoblang. Tajriba asosida aniqlangan uning ebulioskopik konstantasi 3,69 ga teng.

Yechish. Ebulioskopik konstantani hisoblash uchun keltirilgan (VI.30) tenglamadan $\Delta H_{bug'}$ ni topamiz:

$$\Delta H = \frac{R \cdot (T_q)^2 \cdot M_1}{1000 \cdot E} = \frac{8,31 \cdot 10^3 \cdot 458^2 \cdot 18}{1000 \cdot 3,69} = 472 \text{ kJ.}$$

5. 0,01 mol uchmaydigan modda 200 g suvda eritilgan. Suvning ebulioskopik konstantasi 0,512. Eritmaning qaynash haroratini toping.

Yechish. $\Delta T = T - T_{H_2O}$ va $T = T_{H_2O} + \Delta T$.

Bunda T_{H_2O} — suvning, T — eritmaning qaynash harorati. $T_{H_2O} = 373,16$ ga teng. Demak, masalani yechish uchun ΔT ni aniqlash kerak. $\Delta T = E \cdot m$, bunda m — eritmaning molal konsentratsiyasi.

Masala shartiga ko‘ra, 0,01 mol modda — 200 g suvda, m — 1000 g suvda eriganda:

$$m = \frac{0,01 \cdot 1000}{200} = 0,05$$

ga teng bo‘ladi.

Shunga ko‘ra: $\Delta T = 0,512 \cdot 0,05 = 0,0256$.

Endi T_q ni topish mumkin:

$$T = T_{H_2O} + \Delta T = 373,16 + 0,0256 = 373,186 \text{ K.}$$

VI.7. ERUVCHANLIK

a) Gazlarning suyuqliklarda erishi

Gazlar suyuqliklarda ma'lum miqdorda eriydi va bu eruvchanlik gazning xiliga, erituvchi, harorat va parsial bosimga bog'liqdir.

Past bosimda gazlarning eruvchanligi parsial bosimga bog'liqligi Genri qonuni bo'yicha ifodalanadi:

$$N_2 = kP_2. \quad (\text{VI. 32})$$

Gaz bosimi P_2 uning gazdagi konsentratsiyasiga $N_{2,\text{gaz}}$ bog'liqligidan $N_{2,\text{suyuq}} = k N_{2,\text{gaz}}$ kelib chiqadi.

Bunda: N_2 — suyuqlikda erigan gazning molar qismi;

P_2 — eritma ustidagi gazning parsial bosimi;

k — Genri konstantasi.

Agar gaz konsentratsiyasi (C) 1 l eritmadagi grammlar bilan ifodalansa, (VI.32) tenglamani quyidagicha yozish mumkin:

$$C = k^1 P. \quad (\text{VI.33})$$

Bu qonun faqat kichik bosimdagina o'z kuchini saqlaydi. Amalda (VI.32) tenglamadagi eruvchanlikni molar qism (N) bilan emas, balki 1 litr eritmada erigan gaz hajmi (V) birligida ifodalash qabul qilinsa, Genri qonuni quyidagicha yoziladi:

$$V_T = k_p^1 \cdot P_2, \quad (\text{VI.34})$$

bunda: V_T — T haroratda erigan gaz hajmi.

Gazlarning eruvchanligini aniqlashda eruvchanlik koeffitsiyenti (l) dan foydalaniladi:

$$l = k^1 \frac{RT}{M_2}, \quad (\text{VI.35})$$

l — ma'lum haroratda bir hajm eritmada qancha hajm gaz eriganligini ko'rsatadi.

Ideal va o'ta suyultirilgan real eritmalarda gazlarning eruvchanligi bosimga bog'liq emas. Ideal eritmalarda gazlarning eruvchanligi Raul qonuniga ko'ra aniqlanishi mumkin, ya'ni:

$$N_2 = \frac{P_2}{P_2^0}, \quad (\text{VI.36})$$

bunda: N_2 — eritmadagi gazning molar qismi; P_2 — eritma bilan muvozanatda turgan toza gazning bug‘ bosimi; P_2^0 — shu haroratda suyuqlangan gazning to‘yingan bug‘ bosimi.

Agar gaz ideal qonunga bo‘ysunadi, deb faraz qilinsa, Gey-Lyussak qonuniga binoan:

$$\frac{V_T}{V^0} = \frac{T}{T^0} \quad \text{va} \quad \frac{k}{k_{yut}} = \frac{T}{T^0} = \frac{T}{T^0} = \frac{T}{236,16}. \quad (\text{VI.37})$$

$1,013 \cdot 10^5 \text{ N/m}^2$ parsial bosim, normal harorat 273 K da erigan gazning hajmi **adsorbsiya (yutilish)** koefitsiyenti deyiladi. (VI.37) tenglamada V_0 — 273,16 K da erituvchining hajm birligida erigan gaz hajmi ($V_0 = k_{yut} \cdot R_2$), k_{yut} — gazning yutilish koefitsiyenti.

Gazlar eriganda issiqlik ajraladi. Shu sababli Lc-Shatele prinsipi muvofiq harorat ortishi bilan eruvchanlik kamayadi, ya’ni $\frac{\partial N}{\partial T} < 0$. Bu bog‘lanish quyidagicha ifodalanadi:

$$\left(\frac{\partial \ln N}{\partial T} \right)_p = \frac{\Delta H_2}{RT^2}. \quad (\text{VI.38})$$

Agar bu tenglama $T_2 \rightarrow T_1$ oralig‘ida integrallansa:

$$\ln N = - \int_{T_1}^{T_2} \frac{\Delta H_2}{RT^2} \cdot dT. \quad (\text{VI.39})$$

ΔH_2 haroratga bog‘liq bo‘lmasa, ya’ni turg‘un son deb faraz qilinsa, u holda

$$\ln \frac{N_2}{N_1} = \frac{\Delta H_2(T_2 - T_1)}{R \cdot (T_1 \cdot T_2)}, \quad (\text{VI.40})$$

bunda: N_1, N_2 — T_1 va T_2 haroratdagi eruvchanlik. Moddalarning ideal eruvchanligi erituvchi tabiatiga bog‘liq emas. Shreder tenglamasi bo‘yicha ideal eruvchanlikni hisoblash mumkin:

$$\lg N_2 = \frac{\Delta H_e (T - T_{suyuq,2})}{2,3 \cdot R \cdot T_{suyuq,2}}, \quad (\text{VI.41})$$

bunda: N_2 — to'yingan critma hosil bo'lganda cruvchi moddaning molar qismi; $T_{suyuq,2}$ — 1 mol toza cruvchining suyuqlanish harorati; ΔN — 1 mol toza cruvchining suyuqlanish issiqligi; T — qattiq holdagi cruvchining critma bilan muvozanatda turgan harorati.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Kislorodning 298 K da va bosim $399,9 \cdot 10^3 \text{ N/m}^2$ bo'lganda suvdagi cruvchanligi $16 \cdot 10^{-3} \text{ kg/m}^3$ ga teng. Genri koefitsiyentini hisoblang.

Yechish. Gazning cruvchanligi Genri qonuniga binoan (VI.32) tenglama bo'yicha aniqlanadi:

$$N_2 = kr; \quad k = \frac{N_2}{p};$$

$$k = \frac{16 \cdot 10^{-3}}{399,9 \cdot 10^3} = 0,04 \cdot 10^{-5} \text{ kg/N} \cdot \text{m}^2.$$

2. Suv ustidagi gaz aralashmasi hajm birligida 78% N_2 va 22% O_2 dan iborat. Harorat 0°C bo'lganda azotning cruvchanlik koefitsiyenti $l_{N_2} = 0,024$ va kislorodning cruvchanlik koefitsiyenti $l_{O_2} = 0,049$ ga teng. Ergan gaz aralashmasining suyuqlikdagi foiz tarkibini aniqlang.

Yechish. Masalani yechish uchun: 1) 1 m^3 suvda crishi mumkin bo'lgan N_2 va O_2 ning hajm birligidagi miqdorini hisoblaymiz.

(III.32) tenglamaga muvofiq $N_{2,suyuq} = k \cdot N_{2,gaz}$.

Demak, $N_{2,suyuq}$ ni aniqlash uchun N_2 gazining hajmini bilish kerak.

$$V_{N_2} = 0,024 \cdot 0,78 = 0,01872 \text{ m}^3.$$

$$V_{O_2} = 0,049 \cdot 0,22 = 0,01078 \text{ m}^3.$$

Shunga ko'ra, 1 m³ suvda erigan gaz hajmi:

$$0,01872 + 0,1078 = 0,0295 \text{ m}^3;$$

2) suvda erigan gazning foizli tarkibini topamiz:

$$N_{N_2} = \frac{0,01872 \cdot 10001}{0,01872 + 0,078} = \frac{0,01872 \cdot 100}{0,0295} = 63,46\%,$$

$$N_{O_2} = \frac{0,01078 \cdot 100}{0,0295} = 36,54\%.$$

3. 295 K va 51987 N/m² bosimda anilin critmasida H₂S ning cruvchanligi 10,6 kg/m³. Bosim $P = 154628 \text{ N/m}^2$ bo'lganda shu haroratda cruvchanlik 31,6 kg/m³ ga teng. Shunday sharoitda Genri qonuni saqlanib qoladimi?

Y e c h i s h . (VI. 36) tenglamaga muvofiq:

$$k = \frac{P}{N_2}.$$

Gaz fazasi bilan muvozanatda turgan critma bosimining cruvchanlikka nisbati Genri koeffitsiyentiga teng. U esa bosimning o'zgarishiga bog'liq emas. Shunga ko'ra:

$$\frac{51987}{10,6} = 4904,4; \quad \frac{154628}{31,6} = 4893,3.$$

Olingan natijalar shunday sharoitda gazning cruvchanligi Genri qonuniga bo'ysunishini ko'rsatadi (farq 0,2% ni tashkil qiladi).

4. Harorat 0°C va bosim $1,013 \cdot 10^5 \text{ N/m}^2$ bo'lganda asetilenning etanoldagi cruvchanligini hisoblang. Eritmani ideal critma deb hisoblang. Suyuq asetilenning bug' bosimi $26,64 \cdot 10^5 \text{ N/m}^2$. Etanolning zichligi 0,789 g/ml. 0°C va $1,013 \cdot 10^5 \text{ N/m}^2$ bosimda 8 hajm asetilen 1 hajm etanolda criydi.

Y e c h i s h . 1) (VI.36) tenglamaga binoan ideal critmadagi asetilenning molar qismi aniqlanadi:

$$N_{C_2H_2} = \frac{P}{P^0} = \frac{1,013 \cdot 10^5}{26,64 \cdot 10^5} = 0,038.$$

2) 100 g 97% li spirt qancha hajmni egallashini topamiz:

$$V_{sp} = 97/0,789 = 123 \text{ ml.}$$

3) 123 ml spirt da erigan asetilen egallagan hajmni aniqlaymiz:

$$V_{C_2H_2} = 123 \cdot 8,5 = 1045 \text{ ml.}$$

4) spirt dagi asetilenning mol miqdorini topamiz. Asetilenning mol soni:

$$n_{C_2H_2} = \frac{PV}{RT} = \frac{1,013 \cdot 10^5 \cdot 1045 \cdot 10^{-6}}{8,314 \cdot 273} = 0,0467.$$

Etanolning mol soni esa:

$$n_{C_2H_5OH} = \frac{g}{M} = \frac{97}{46} = 2,11.$$

Shulardan foydalanib, asetilenning eritmadagi eruvchanligi molar qismini hisoblaymiz:

$$N_{C_2H_2} = \frac{0,0467}{2,11 + 0,0467} = 0,022.$$

Asetilenning eruvchanligidagi bunday farq ($0,16 = 0,038 - 0,022$) uning spirt dagi eritmasi ideal eritma deb hisoblanishi mumkin emasligini ko'rsatadi.

b) Qattiq moddalarning suyuqliklarda erishi

Qattiq moddalarning suyuqliklardagi eruvchanligi to'yingan eritma konsentratsiyasi bilan o'lchanadi. Qattiq moddalarning harorat ta'sirida suyuqliklarda erishi Shreder tenglamasi orqali ifodalanadi:

$$\frac{d \ln N}{dT} = \frac{\Delta H}{RT^2}, \quad (\text{VI.42})$$

bunda: N — to'yingan eritma konsentratsiyasi;

ΔH — yashirin suyuqlanish (erish) issiqligi.

Demak, harorat ortishi bilan qattiq moddalarning suyuqlikda erishi ko'payadi. ΔH harorat ortishi bilan o'zgarmaydi, ya'ni

turg'un son deb faraz qilinib, (VI.42) tenglama integrallansa, quyidagiga ega bo'lamiz:

$$\ln N = B - \frac{\Delta H}{R} \cdot \frac{1}{T}. \quad (\text{VI.43})$$

B — integrallash doimiysi. Agar koordinataning ordinata o'qiga $\ln N$ va absissa o'qiga $\frac{1}{T}$ qiymatlari qo'yilsa, $\ln N - \frac{1}{T}$ bog'lanishida to'g'ri chiziq grafigi olinadi. (VI.42) tenglama N_1, N_2 eruvchanlik qiymatlari bo'yicha T_1 va T_2 chegarasida integrallansa:

$$\ln \frac{N_2}{N_1} = \frac{\Delta H (T_2 - T_1)}{R \cdot (T_2 \cdot T_1)} \quad \text{yoki} \quad \lg N_2 / N_1 = \frac{\Delta H \cdot (T_2 - T_1)}{2,3 R \cdot (T_2 \cdot T_1)}.$$

MASALALAR YECHISHIGA DOIR MISOLLAR

1. o - dinitrobenzol (1) va m - dinitrobenzol (2) aralashmasida 64°C da aralashma ($N_1 = 0,65$) da ularning qattiq holati bilan muvozanatda bo'ladi. o - dinitrobenzol va m - dinitrobenzolning suyuqlanish issiqqligi mos ravishda 130,2 va 100,7 J/g ga teng. Dinitrobenzolning molekular massasi $M = 168$. Toza komponentlarning suyuqlanish haroratini aniqlang.

Yechish. (VI.41) tenglamadan:

$$T_{\text{suyuq},1} = \frac{\Delta H_{\text{suyuq}} \cdot T}{2,3 R T \lg N_1 + \Delta H_{\text{suyuq},1}} = \frac{130,2 \cdot 168 \cdot 337}{19,1 \cdot 337 \lg 0,65 + 130,2 \cdot 168} = 390 \text{ K},$$

$$T_{\text{suyuq},2} = \frac{\Delta H_{\text{suyuq},2} \cdot T}{2,3 R T \lg N_2 + \Delta H_{\text{suyuq},2}} = \frac{100,7 \cdot 168 \cdot 337}{19,1 \cdot 337 \lg 0,35 + 100,7 \cdot 168} = 363 \text{ K}.$$

VI.8. TAQSIMLANISH QONUNI VA EKSTRAKSIYA

Amalda bir-birida erimaydigan ikki suyuqlik qatlamidan iborat sistemaga uchinchi modda qo'shilsa, bu modda ikki qatlam bo'ylab shu sharoitda o'zaro taqsimlanadi. Taqsimlanish qonuniga ko'ra, **taqsimlanish koeffitsiyenti** (K) suyultirilgan eritmalar uchun

$$K = \frac{C_1}{C_2} \quad (\text{VI.44})$$

ga teng.

Bunda: C_1 , C_2 — taqsimlanayotgan moddaning birinchi va ikkinchi qatlamdagi konsentratsiyasi; K — taqsimlanish koeffitsiyenti.

K ning qiymati haroratga, crituvchi va eruvchi moddalar tabiatiga, xossalariga bog'liq. Demak, muvozanat holatida uchinchi moddaning ikkala qatlamdagi konsentratsiyasi orasidagi nisbat o'zgarmas haroratda doimiy kattalikdir.

Eritmalarda erigan modda konsentratsiyasi o'rniga aktivlik qiymati qo'llanilsa:

$$K^I = \frac{a_1}{a_2}. \quad (\text{VI.45})$$

(VI.44) va (VI.45) tenglamalar Nernstning taqsimlanish qonuni ifodasidir.

Agar taqsimlanayotgan (uchinchi) modda crituvchilardan birida dissotsilansa yoki assotsilansa, buni e'tiborga olgan holda taqsimlanish qonuni quyidagicha ifoda etiladi:

$$K'' = K_D K^I = \frac{C_2^n}{C_1}. \quad (\text{VI.46})$$

Bu Shilovning taqsimlanish qonunidir. K_D — dissotsilanish konstantasi, n — dissotsilanish natijasidagi zarrachalar sonining o'zgarishi. Agar $AB \rightarrow A + B$ jarayoni borayotgan bo'lsa $n = 2$, $2AB \rightarrow (AB)_2$ jarayoni borayotgan bo'lsa, $n = \frac{1}{2}$ ga teng bo'ladi. Bir-birida aralashmaydigan ikki suyuqlikda taqsimlanayotgan uchinchi moddaning dissotsilanish darajasi (α) turli crituvchilarda har xil qiymatga ega bo'ladi. Agar taqsimlanayotgan moddani birinchi crituvchidagi dissotsilanish darajasi α_1 , ikkinchida α_2 bo'lsa, u holda taqsimlanish qonuni tenglamasi

$$K = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)} \quad (\text{VI.47})$$

bo'ladi.

Moddalarni bir suyuqlikdan yoki qattiq moddalardan boshqa crituvchi (ekstragent) yordamida ajratib olishga **ekstraksiya** deyiladi. Ekstraksiya sanoatda keng qo'llaniladi. Masalan, benzol

(ekstragent) yordamida chigitdan yog‘ ajratib olinadi. Ekstraksiyani bir necha bosqichda olib borish mumkin (*parsiyal, ya’ni bo‘lingan holda ekstraksiya*).

Erituvchining V_1 hajmida q_0 g ekstraksiya qilinadigan modda bo‘lsin. Unga V_2 hajm ekstragent qo‘shib ekstraksiya jarayoni olib borilganda birinchi erituvchida q_1 modda qoladi.

Bunda ekstragentga ($q_0 - q_1$) g modda o‘tadi. Demak, birinchi erituvchida va ekstragentda modda konsentratsiyalari:

$$C_1 = \frac{q_1}{V_1}; \quad C_2 = \frac{q_0 - q_1}{V_2}. \quad (\text{VI.48})$$

Bu qiymatlar (VI.46) ga qo‘yilsa:

$$K^1 = \frac{C_1}{C_2} = \frac{q_1 V_2}{V_1 (q_0 - q_1)}. \quad (\text{VI.49})$$

Bundan:

$$q_1 = q_0 \frac{K^1 V_1}{K^1 V_1 + V_2}. \quad (\text{VI.50})$$

Agar birinchi eritma yana shu miqdordagi V_2 , ekstragentning yangi porsiyasi bilan ekstraksiya qilinsa, birinchi erituvchida ekstraksiya qilinmasdan qolgan modda q_2 bo‘ladi, ya’ni:

$$q_2 = q_1 \frac{K^1 V_1}{K^1 V_1 + V_2} = q_0 \left(\frac{K^1 V_1}{K^1 V_1 + V_2} \right)^2. \quad (\text{VI.51})$$

Agar bu jarayon n marta takrorlansa, ekstraksiya qilinmasdan qolgan modda miqdori q_n bo‘ladi, u holda:

$$q_n = q_0 \left(\frac{K^1 V_1}{K^1 V_1 + V_2} \right)^n, \quad (\text{VI.52})$$

n — ekstraksiya qilingandan so‘ng qolgan modda miqdori $q_e = q_0 - q_n$ bo‘ladi, unda ekstraksiya natijasida ajratib olinayotgan modda miqdori quyidagi tenglama orqali aniqlanadi:

$$q_e = q_0 \left[1 - \left(\frac{K^1 V_1}{K^1 V_1 + V_2} \right)^n \right]. \quad (\text{VI.53})$$

Agar porsiyalab ekstraksiya qilinmasdan hamma ekstragent nV_2 bilan bir yo‘la ekstraksiya qilinsa:

$$q_e = q_0 \left[1 - \frac{K_1^1 V_1}{K^1 V_1 + V_2} \right] \quad (\text{VI.54})$$

teng bo'ladi.

Demak, bor ekstragent bilan bir yo'la emas, balki porsiyalab ekstraksiya qilinganda ko'p miqdorda modda ekstraksiya qilinadi.

MASALALAR YECHISHGA DOIR MISOLLAR

1. Pikrin kislotaning 0,02 *m* suvli eritmasi benzolda erigan 0,07 *m* pikrin kislota eritmasi bilan muvozanatda turibdi. Pikrin kislota suvda qisman dissotsilanadi va uning dissotsilanish darajasi 0,9 ga teng bo'ladi. Pikrin kislotaning benzol va suv qatlamlarida taqsimlanish koeffitsiyenti hisoblansin.

Yechish. Masalani yechish uchun (VI.47) tenglamadan foydalanamiz, ya'ni:

$$K = \frac{0,07}{0,02(1-0,9)} = 35.$$

2. Yodning suv va uglerod (IV) sulfid (CS_2) da taqsimlanish koeffitsiyenti 0,0017 ga teng. Tarkibida 1 g/l yod bo'lgan suvli eritma uglerod (IV) sulfid bilan chayqatiladi. Agar:

1) 1 l yodning suvli eritmasi 0,05 l uglerod (IV) sulfid eritmasi bilan chayqatilayotgan bo'lsa;

2) 1 l yodning suvli eritmasiga uglerod (IV) sulfidning 5 marta 0,001 l hajmli eritmasidan alohida-alohida solish bilan chayqatib, suvli eritmada qolgan yodning miqdorini toping.

Yechish. (VI.50) tenglama bo'yicha $n = 1$ bo'lgandagi q_1 ni (ekstraksiya qilingan) topamiz:

$$q_1 = 1 - \frac{0,0017 \cdot 1}{0,0017 \cdot 1 + 0,05} = \frac{0,0017}{0,0517} = 0,033.$$

Demak, ekstraksiya natijasida $q_2 = q_0 - q_1 = 1,000 - 0,033 = 0,967$ g modda ajratib olingan.

(VI.52) tenglama bo'yicha $n = 5$ ga teng bo'lgandagi q_5 ni (ekstraksiyalanmagan) hisoblaymiz:

$$q_5 = 1 - \left[\frac{0,0017 \cdot 1}{0,0017 \cdot 1 + 0,01} \right]^5 = \left[\frac{0,0017}{0,0117} \right]^5 = [0,145]^5 = 6,45 \cdot 10^{-5} \text{ g.}$$

Demak, 5 marta ekstraktsiya qilingandan so'ng yod deyarli 100% ekstraktsiya qilingan.

VI.9. REAL ERITMALAR. TERMODINAMIK AKTIVLIK

Real eritmalar ideal va cheksiz (yoki o'ta) suyultirilgan eritmalariga xos tarkib bilan eritma xossasini bog'lovchi tenglamalarga bo'ysunmaydi, ya'ni chetlanadi. Real eritmalar xossasi eritma konsentratsiyalaridan tashqari eritmaning tarkibiy qismlari orasidagi o'zaro ta'sirlanishlarga ham bog'liq. Konsentratsiya bilan bir qatorda shu ta'sirlanishni e'tiborga olgan va xossalarida to'liq namoyon bo'ladigan konsentratsiya ifodasiga **termodinamik aktivlik** (a) deyiladi.

Real eritmalar xossasi bilan eritma tarkibi orasidagi bog'lanish Lyuisning real eritmalar nazariyasiga ko'ra quyidagicha ifodalanadi:

$$a_i = \gamma \cdot C_i \quad \text{yoki} \quad a_i = \gamma \cdot m_i; \quad a_i = \gamma \cdot N_i, \quad (\text{VI.55})$$

bunda: a — termodinamik aktivlik; γ — termodinamik aktivlik koeffitsiyenti; C, m, N — konsentratsiya (turli ifodalarda — molar, mol/l, molar qism).

Ideal va cheksiz suyultirilgan eritmalarda $a = c$, $\gamma = 1$ bo'ladi. Demak, γ — zarrachalar orasidagi o'zaro ta'sir kuchlarini aks ettiradi va eritma konsentratsiyasiga bog'liq holda o'zgaradi. Real eritmalar uchun Raul qonuni ifodasi quyidagicha bo'ladi:

$$P_1 = P_1^0 a_1; \quad P_2 = P_2^0 a_2. \quad (\text{VI.56})$$

Real eritmalariga termodinamik tenglamalarni qo'llash uchun ideal va cheksiz suyultirilgan eritmalariga mansub eritma tarkibi bilan bog'liq tenglamalarda konsentratsiya o'rniga termodinamik aktivlik (a) ifodasini qo'llash kerak.

Real gazlarda bosim ifodasi o'rniga izotermik funksiya — f , ya'ni **uchuvchanlik** qo'llaniladi. Uchuvchanlik va bosim o'zaro quyidagicha bog'langan:

$$f_i = \gamma P, \quad (\text{VI.57})$$

bunda γ — uchuvchanlik koeffitsiyenti, uchuvchanlik quyidagi tenglama asosida aniqlanishi mumkin:

$$RT \ln f = RT \ln P - \int_0^P \Delta V \cdot dP,$$

bunda: f — uchuvchanlik; P — bosim; $\Delta V = V_{id} - V$ (V_{id} — gaz ideal gaz bo'lganda ma'lum harorat va bosimda ishg'ol qilgan hajmi, V — ma'lum harorat va bosimda amalda ishg'ol qilgan hajmi).

Agar V va P ning bog'lanishi ma'lum bo'lsa, $\int_0^P \Delta V \cdot dP$ grafik usul bilan aniqlanishi mumkin.

Uchuvchanlikni taqriban (taxminiy) quyidagi tenglama bilan aniqlash mumkin:

$$f = \frac{P^2}{P_{id}}, \quad (\text{VI.58})$$

P_{id} — gaz ideal bo'lganda ma'lum harorat va hajmdagi bosimi. P — haqiqiy bosimi.

Real critmalardagi erigan modda aktivligi muzlash haroratining pasayishi orqali aniqlanishi mumkin:

$$-\ln \frac{a_2}{m} = \int_0^m \frac{j}{m} dm + j. \quad (\text{VI.59})$$

$$\text{Bunda:} \quad j = 1 - \frac{\Delta T_{muz}}{E \cdot m}, \quad (\text{VI.60})$$

$\Delta T_{muz.} = T^0 - T$, m — mol konsentratsiya, E — ebullioskopik konstanta.

Juda suyultirilgan eritmalar uchun (VI.59) tenglama quyidagicha bo'ladi:

$$\ln \gamma = \ln \frac{a_2}{m} = -2j. \quad (\text{VI.61})$$

Erituvchining eritmada bug' bosimini o'lchash bilan eruvchining termodinamik aktivligini (yoki koeffitsiyenti γ ni) Gibbs-Dyugem tenglamasi yordamida aniqlash mumkin:

$$\lg a_2 = \lg a_2^1 + \int_{a_1^1}^{a_1} \frac{N_1}{N_2} (-\lg a_1), \quad (\text{VI.62})$$

$$\lg \gamma_2 = \lg \gamma_2^1 + \int_{\gamma_1^1}^{\gamma_1} \frac{N_1}{N_2} (-\lg \gamma_1). \quad (\text{VI.63})$$

Bunda a_1, a_2 (γ_1, γ_2) — erituvchi va eruvchining N_1^1 konsentratsiyadagi termodinamik aktivligi (yoki aktivlik koeffitsiyenti). Integralni yechish uchun a_1^1, a_2^1 (yoki γ_1^1, γ_2^1) ma'lum bo'lishi kerak.

(VI.62) va (VI.63) tenglamadagi integrallar grafik usul bilan « $\frac{N_1}{N_2} - \lg a_1$ yoki $\frac{N_1}{N_2} - \lg \gamma_2$ » bog'lanishlar orqali topiladi.

Aktivlik qiymatini bilgan holda real eritmalar uchun muvozanat holatdagi xossalarni quyidagicha ifodalash mumkin:

$$\text{Raul qonuni } P = aP^0; \quad \text{Genri qonuni } P_i = \gamma \cdot a_p, \quad (\text{V.64})$$

bu tenglamada P — osmotik bosim; V — erituvchining molar hajmi.

Ayrim hollarda aktivlik koeffitsiyenti o'rniga osmotik koeffitsiyent (k) qo'llaniladi. Aktivlik koeffitsiyenti va osmotik koeffitsiyent orasida quyidagicha bog'lanish mavjud:

$$\lg \gamma_i = (k - 1) \cdot \lg N_i, \quad (\text{VI.65})$$

osmotik bosim koeffitsiyenti (k):

$k = \frac{\pi}{\pi_{id}}$; π, π_{id} — real va ideal eritmalarining osmotik bosimi; k — real eritma osmotik bosimining ideal eritma osmotik bosimidan farqini ko'rsatadi. Doimo $k > 1$ bo'ladi.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Uchuvchan bo'lmagan moddaning suvli eritmasidagi molar qismi 0,07 ga teng. Agar uning eritma ustidagi bug' bosimi $26,17 \cdot 10^2$ Pa bo'lsa, 298 K dagi suvning aktivlik koeffitsiyentini toping. Toza suv ustidagi to'yingan bug' bosimi $32,17 \cdot 10^2$ Pa ga teng.

Yechish. Suvning termodinamik aktivligi (VI.55) tenglamaga muvofiq quyidagicha aniqlanadi. Raul qonuniga binoan $P_1 = aP_1^o$:

$$a = \frac{P_1}{P_1^o} = \frac{26,17 \cdot 10^2}{32,17 \cdot 10^2} = 0,8.$$

Suvning eritmadagi molar qismi topiladi:

$$N_{H_2O} = 1 - 0,07 = 0,93.$$

Eritmaning aktivlik koeffitsiyenti quyidagicha topiladi:

$$\gamma = \frac{a}{N_{H_2O}} = \frac{0,8}{0,93} = 0,86.$$

2. Glitserinning 0,1 mol eritmasi — 0,2°C da muzlaydi. Suvning krioskopik konstantasi 1,86. Glitserin eritmasining aktivligini aniqlang.

Yechish. (VI.63) tenglama orqali j ni topamiz:

$$j = 1 - \frac{\Delta T_{muz}}{K \cdot m} = 1 - \frac{0,2}{1,86 \cdot 0,1} = -0,075.$$

(VI.64) tenglama yordamida aktivlik koeffitsiyentini hisoblaymiz:

$$\lg \gamma = -\frac{2j}{2,3} = -\frac{2 \cdot 0,075}{2,3} = 0,067.$$

$$\gamma = 1,16.$$

Demak, aktivlik $a = 1,16 \cdot 0,1 = 0,116$.

3. Binar eritmada erigan moddaning molar qismi 0,5 ga, aktivlik koeffitsiyenti 0,8 ga teng. Osmotik koeffitsiyentni toping.

Yechish. (VI.72) tenglamadan foydalanib osmotik koeffitsiyentni topamiz:

$$\lg \gamma_i = (k - 1) \cdot \lg N_i .$$

$$\text{Bundan } k = 1 + \frac{\lg N}{\lg N_i} = 1 + \frac{\lg 0,8}{\lg 0,5} = 1 + \frac{(-0,0969)}{(-0,3010)} = 1,32.$$

4. Toza asetonning 298,2 K dagi bug' bosimi $P^o = 372,4$ mm simob ustuniga teng. Tarkibida aseton (2) bo'lgan eritma ustidagi xloroform (I) bug' bosimi tarkib bilan quyidagicha o'zgaradi:

N_1 , molar qismi	0,4	0,5	0,6	0,7	1,0
P_1 , mm sim.ustuni	105	147	194	242	372

0,5 molar qism asetoni bor eritmaning aktivlik koeffitsiyenti — γ_2 ni aniqlang. Bunda 0,34 molar qism asetoni bor eritmaning aktivlik koeffitsiyenti $\gamma_2^I = 0,49$ ga teng.

Y e c h i s h . Asetonning aktivlik koeffitsiyentini (VI.63) tenglama bo'yicha aniqlaymiz. Tenglama integralini grafik usul orqali hisoblaymiz. Koordinatalarning absissa o'qiga $\lg \gamma_1$ va ordinata o'qiga N_1/N_2 qiymatlari qo'yiladi (VI.3-rasm). Grafik tuzish uchun avval N_1/N_2 va $\lg \gamma_2$ qiymatlari topiladi. Agar $N_1 = 0,4; 0,5; 0,6; 0,7$ bo'lsa, u holda $N_2 = 1 - N_1$ 0,6; 0,5; 0,4; 0,3 ga teng bo'ladi. Unda $N_1/N_2 = 0,67; 1,0; 1,50; 2,33$ bo'ladi, u holda

$$a_1 = P_1 / P_1^o = \frac{P_1}{372} = 0,282; 0,395;$$

$$0,522; 0,651. \text{ Shunga ko'ra,}$$

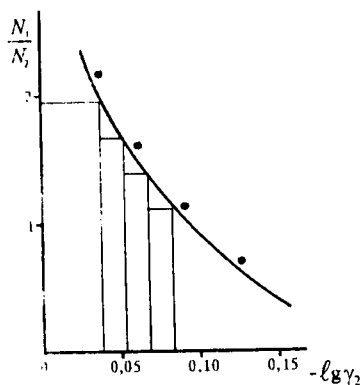
$$\gamma_1 = a_1 / N_1 = 0,705; 0,790; 0,870;$$

$$0,930 \text{ yoki } \lg \gamma_1 = 0,151; 0,102;$$

$$0,060; 0,032 \text{ ga teng bo'ladi.}$$

Olingan natijalar bo'yicha grafik chizamiz.

$N_2 = 0,34$ yoki $N_1/N_2 = 0,66/0,34 = 1,94$; $N_2 = 0,5$ yoki $N_1/N_2 = 0,5/0,5 = 1$ qiymatlar bo'yicha egri chiziq ostidagi yuzalarni hisoblaymiz. Olingan mas-



VI.3-rasm. Grafik usul bilan (VI.63) tenglama integralini aniqlash.

shtablarda bu yuza 2160 mm^2 ga teng bo'лади. Shunga ko'ra, 2 birlikda $N_1/N_2 100 \text{ mm}$; $1 \text{ mm} = 2 \cdot 10^{-2}$ birlikka; $0,2$ birlik — $\lg \gamma_1 100 \text{ mm}$; $1 \text{ mm} = 2 \cdot 10^{-2}$ birlikka teng bo'лади. Demak, 1 mm^2 da $4 \cdot 10^{-5}$ da birlik mavjud.

Shunday qilib, (VI.66) tenglama bo'yicha quyidagilarni aniq-laymiz:

$$\lg \gamma_2 - \lg 0,49 = 2160 \cdot 4 \cdot 10^{-5} = 0,087,$$

$$\lg \gamma_2 = 0,087 - 0,308 - 0,221 = 1,779,$$

$$\gamma_2 = 0,60 \text{ va } a_2 = 0,60 \cdot 0,50 = 0,30 \text{ ga teng.}$$

5. 60°C va 50 atm. bosimda 1 mol NH_3 $0,467 \text{ l}$ hajmni ishg'ol qiladi. Shu sharoitda NH_3 ning uchuvchanligini aniqlang.

Y e c h i s h . Uchuvchanlik (VI.58) tenglama bilan aniqlanadi:

$$f = \frac{P_2}{P_{id}}.$$

Klayperon tenglamasi $PV = nRT$ yordamida P_{id} aniqlanadi:

$$P_{id} = \frac{nRT}{V} = \frac{1,0,0821,333}{0,467} = 58,53$$

va

$$f = \frac{P^2}{P_{id}} = \frac{50^2}{58,53} = 42,71.$$

6. 0°C da kislorodning mol hajmi bosim bo'yicha quyidagicha o'zgaradi:

$P, \text{ atm.}$	1	50	100	200	500
$V, \text{ l}$	22,4	0,4280	0,2076	0,1024	0,0519

320 va 200 atm. da, 0°C da kislorodning uchuvchanligini aniqlang.

Y e c h i s h . (VI.57) tenglama

$$RT \ln f = RT \ln P - \int_0^P \Delta V dP$$

dan foydalaniladi. $\Delta V = V_{id} - V$; V_{id} — Klayperon tenglamasi bilan topiladi:

P , atm.	1	50	100	200	500
V_{id} , l	22,4	0,4482	0,2241	0,1121	0,0448
ΔV , l	0	0,0202	0,0165	0,1097	-0,0071

ΔV ning P ga bog‘liq ravishda o‘zgarish grafigi tuziladi va bu grafikdan:

$$\int_0^{320} \Delta V dP = 4,1; \quad \int_0^{200} \Delta V dP = 3,3,$$

yuqoridagi (VI.57) tenglamaga bu qiymatlar qo‘yilsa, $P = 320$ atm. uchun:

$$0,0821 \cdot 273 \cdot 2,3 \lg f = 0,0821 \cdot 273 \cdot 2,3 \lg 320 - 4,1,$$

$$\lg f = \lg 320 - \frac{4,1}{51,54}; \quad f = 266,4.$$

Xuddi shunday $P = 200$ atm. bosim uchun: $f = 172,6$.

MASALALAR

1. Eritma 50% H_2O , 35% C_2H_5OH va 15% CH_3COOH dan iborat. Komponentlarning molar qismini toping.

2. 50% li $AgNO_3$ ning suvli eritmasi uchun (zichligi 1,668 g/ml) $20^\circ C$ da molar qismi va normal konsentratsiya ifodasini aniqlang.

3. Konsentratsiyasi 30% bo‘lgan $CaCl_2$ ($d = 1,282$ g/ml) suvli eritma uchun molar qismi va normal konsentratsiya ifodasini toping.

4. 200 g benzol, 100 g etil spirti va 50 g asetonni o‘zaro aralashtirib eritma hosil qilingan. Shu eritma komponentlarining molar qismi qanchaga teng?

5. 10% li $NaCl$ eritmasining zichligi $1,071$ g/sm³ ga teng. Eritma tarkibidagi tuzning 1000 g suvdagi molar qismini toping.

6. Konsentratsiyasi 10% bo‘lgan sulfat kislota eritmasining molar va molar qism ifodasidagi konsentratsiyalarini aniqlang.

7. Tarkibida 1,405 mol/l miqdorda AgNO_3 erigan eritmaning molar qismi, foiz, molal va normal konsentratsiyasini toping. Eritmaning 20°C dagi zichligi 1,194 g/ml ga teng.
8. Zichligi 20°C da 1,05 g/ml ga teng HCl ning eritmada molar qismi 0,05 ga teng. Shu eritmaning foiz, molar, molal va normal konsentratsiyalarini hisoblang.
9. 2,31% li NH_3 eritmasining zichligi $0,99 \text{ g/sm}^3$ ga teng. Eritmaning molal, molar konsentratsiyasi va molar qismini toping.
10. 20°C da zichligi 1,045 bo'lgan 4,462% li CuSO_4 eritmasining molar va molal konsentratsiya qiymatini aniqlang.
11. 60% li ortofosfat kislota eritmasining 293 K dagi zichligi 1426 kg/m^3 ga teng. H_3PO_4 ning molar qismi, molal va molar konsentratsiyalarini toping.
12. Konsentratsiyasi 1,65 mol/1000 g bo'lgan FeSO_4 eritmasining zichligi 1,213 g/ml ga teng. Eritmaning molar qismi, foiz, molar va normal konsentratsiyasini hisoblang.
13. Konsentratsiyasi 30% bo'lgan AlCl_3 eritmasining 293 K dagi zichligi 1,242 g/ml ga teng. Eritmaning molar qismi, molal, molar va normal konsentratsiyasini aniqlang.
14. Metil spirti CH_3OH ning 20% suvli eritmasi zichligi $0,9681 \text{ g/sm}^3$ ga teng. Eritmaning molar, molal konsentratsiya qismini toping.
15. KCl eritmasida 250 g KCl va 1000 g H_2O bor. Eritma zichligi $1,133 \text{ g/sm}^3$. Eritmaning molar qismi, molar, molal va foiz konsentratsiyasini toping.
16. 20 g NH_4NO_3 100 g eritmada eritilgan. Suvli ammoniy nitrat (NH_4NO_3) eritmasining hajmi $92,35 \text{ sm}^3$, erituvchi hajmi $80,14 \text{ sm}^3$ ga teng. NH_4NO_3 ning eritmadagi parsial mol hajmini toping.
17. Tarkibida 35 g NH_4NO_3 bo'lgan 100 g eritmaning hajmi $86,87 \text{ sm}^3$ va erituvchi hajmi $57,5 \text{ sm}^3$ ga teng. NH_4NO_3 eritmasining parsial mol hajmini hisoblang.
18. Metil spirtining 60% li suvli eritmasining 293 K dagi zichligi $0,8946 \text{ g/sm}^3$ ga teng. Suvning eritmadagi parsial mol hajmi $16,8 \text{ sm}^3/\text{mol}$. Spirtning parsial mol hajmini aniqlang.

19. Konsentratsiyasi 20% bo'lgan metil spirti eritmasida suvning parsial mol hajmi $18 \text{ sm}^3/\text{mol}$, spirtniki $37,8 \text{ sm}^3/\text{mol}$ ga teng. Eritmaning mol hajmini toping.

20. Quyidagi ma'lumotlar asosida grafik usul bilan eritmadagi FeCl_3 ning parsial mol hajmini aniqlang. Eritmaning molalligi $m = 0,4$ ga teng.

100 g suvdagi FeCl_3 ning mol soni	0,0000	0,0126	0,0257	0,0394	0,0536
100 g suv tutgan eritma hajmi	100,13	100,58	100,98	101,38	101,73

21. Tarkibida 30% NH_3 bo'lgan suvli eritma zichligi $0,8951 \text{ g/sm}^3$, suvning parsial mol hajmi 18 sm^3 ga teng. Ammiakning eritmadagi parsial mol hajmini toping.

22. Molalligi $m = 0,3$ bo'lgan eritmadagi CuSO_4 parsial mol hajmini grafik usul bilan quyidagi natijalar asosida toping:

Eritmadagi CuSO_4 , %	1,912	3,187	4,462	5,737
Eritma zichligi, g/sm^3	1,0190	1,0319	1,0450	1,0582

23. 1000 g suvda erigan NaCl eritmasi hajmi tuzning mol soni bilan quyidagi tenglama bo'yicha bog'langan:

$$V = 1000 + 16,4 n_2 + 2,5n_2^2 - 1,2n_2^3.$$

Molalligi $m = 0,5$ bo'lgan eritmadagi NaCl ning parsial mol hajmini toping.

24. Talliy (2) — simob (1) dan 298 K da va N_2 konsentratsiyada 1 kg eritma hosil bo'lganda quyidagi berilgan ma'lumotlardan foydalanib, parsial mol entalpiya, izobarik potentsial va entropiyaning o'zgarishini aniqlang. $N_2 = 0,050$ (talliy atomi miqdori):

$$\begin{aligned} \Delta \overline{G}_1 &= -154,8 \text{ J/mol}; & \Delta \overline{G}_2 &= -9000 \text{ J/mol}, \\ \Delta \overline{S}_1 &= 0,25 \text{ J/mol} \cdot ^\circ\text{C}; & \Delta \overline{S}_2 &= 22,01 \text{ J/mol} \cdot \text{grad}. \end{aligned}$$

25. Tarkibida 62% Cu bo'lgan qotishmaning mol hajmini toping. Mis zichligi $8,9 \text{ g/sm}^3$ ga, ruxniki esa $7,1 \text{ g/sm}^3$ ga teng. Qotishma hajmi, tarkibiy qismlar addetivdir.

26. 1 mol HCl ning 3 mol H_2O da erigandagi erish issiqligini hisoblang. Bunda H_2O ning parsial mol entalpiya o'zgarishi $36,28 \text{ kJ/mol}$, HCl niki $-5,77 \text{ kJ/mol}$ ga teng.

27. 1 mol HCl ning 10 mol H_2O da erigandagi erish issiqligini hisoblang. Bunda H_2O ning parsial mol entalpiyasi o'zgarishi $11,38 \text{ kJ/mol}$, HCl niki $4,18 \text{ kJ/mol}$ ga teng.

28. 1 mol HCl ning 50 mol H_2O da erigandagi erish issiqligini hisoblang. Bunda H_2O ning parsial mol entalpiyasi o'zgarishi $3,29 \text{ kJ/mol}$, HCl niki $0,00 \text{ kJ/mol}$ ga teng.

29. 1 mol ZnCl_2 ning 13 mol H_2O da erigandagi $\Delta H_e = 10000 \text{ kJ/mol}$. 5 kg shunday modda suyultirilganda qancha miqdorda issiqlik ajralib chiqadi? ZnCl_2 ning bunday suyultirilgan eritmasi hosil bo'lishida $\Delta H_e = 12500 \text{ kJ/mol}$ ga teng.

30. 1 mol HCl ning 1600 mol H_2O da erish issiqligini toping. Bunda H_2O ning parsial mol entalpiyasi $0,60 \text{ kJ/mol}$, HCl $0,01 \text{ kJ/mol}$ ga teng.

31. 77,8% li azot kislotasi 25,9% gacha suyultirilganda issiqlik effektini toping. Hisoblashlar uchun ilovada keltirilgan ma'lumotlardan foydalaning.

32. 0,3 kg suvga 50% li H_2SO_4 dan 0,1 kg qo'shilganda ajralib chiqqan issiqlikni aniqlang. Hisoblashlar uchun ilovada keltirilgan ma'lumotlardan foydalaning.

33. 0,5 kg 20% li H_2SO_4 ga 1 kg 60% li H_2SO_4 eritmasi qo'shilganida ajralib chiqqan issiqlik miqdorini toping. Hisoblar uchun ilovada keltirilgan ma'lumotlardan foydalaning.

34. 100 g 80% li H_2SO_4 ni 500 g suvda suyultirilganda ajralgan issiqlikni hisoblang. Hisoblashlar uchun ilovada keltirilgan ma'lumotdan foydalaning.

35. 1,5 g LiCl 10 g LiCl ning suvli (30%) eritmasida erigandagi issiqlikni aniqlang (ilovada keltirilgan ma'lumotdan foydalaning).

36. 5 g CH_3COOH ning 100 g 32% li shu kislota eritmasiga qo'shilgandagi erish issiqligini toping (ilovadagi ma'lumotdan foydalaning).

37. 50 g 20% li NaOH eritmasining 50 g 40% li NaOH eritmasi bilan aralashgandagi issiqlik effektini hisoblang (ilovadagi ma'lumotlardan foydalaning).

38. BaCl_2 ning suvda erish issiqligi 2070 kal/mol ga teng. $\text{BaCl}_2 \times 2\text{H}_2\text{O}$ hosil bo'lishida gidratlanish issiqligi 6970 kal/mol $\times \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ning erish issiqligi nimaga teng?

39. CuSO_4 ning erish issiqligi 15800 kal/mol. Gidratlangan $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ning erish issiqligi 2750 kal/mol ga teng. $\text{CuSO}_4 + 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ reaksiyasining issiqligini toping.

40. CHCl_3 ning CCl_4 da erish integral issiqligi tarkibiga nisbatan quyidagicha bog'langan:

CHCl_3	0,1822	0,2705	0,4589	0,5669	0,0377	0,7572	0,8850
ΔH , kJ/mol eritmada	-0,146	-0,185	-0,226	-0,228	-0,219	-0,176	-0,103

ΔH ning N_{CHCl_3} bo'yicha grafigini chizib, CHCl_3 ning molar qismi $N_{\text{CHCl}_3} = 0,44$ bo'lgan eritmada komponentlarning differensial erish issiqliklarini aniqlang.

41. 298 K da konsentratsiyasi 25% bo'lgan glukoza ($\text{C}_6\text{H}_{12}\text{O}_6$) eritmasi ustidagi bug' bosimini hisoblang. Bunda erituvchi — toza suvning shu haroratdagi to'yingan bug' bosimi $3,721 \cdot 10^3$ Pa ga teng.

42. Dibrompropan ($\text{C}_3\text{H}_6\text{Br}_2$) va dibrometan ($\text{C}_2\text{H}_4\text{Br}_2$) ning 360 K dagi to'yingan bug' bosimlari mos ravishda 130 va 172 mm simob ustuniga teng. Bu modda eritmalari Raul qonuniga bo'ysunadi. Eritmaning konsentratsiyasi 50% bo'lgandagi umumiy bug' bosimini toping.

43. Suv bug'i bosimi 25°C da 23,76 mm sim. ustuniga teng. 6 g mochevina 180 g suvda erishidan hosil bo'lgan eritma ustidagi bug' bosimini aniqlang.

44. Etil efirining 20°C dagi bug' bosimi 442 mm sim. ustuniga teng. 100 g efirda 15 g benzaldegidning erishidan hosil bo'lgan eritmaning to'yingan bug' bosimini aniqlang.
45. Suvning 25°C dagi bug' bosimi 23,76 mm simob ustuniga teng. 5% li shakar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) eritmasining bug' bosimini aniqlang.
46. 10% li glitserin ($\text{C}_3\text{H}_8\text{O}_3$) eritmasining bug' bosimini hisoblang. Suv bug'i bosimi 23,8 mm simob ustuniga teng.
47. 293 K da etil efirda erib 3% li eritma hosil qilgan anilin eritmasining bug' bosimini toping. Shu haroratda toza efirning bug' bosimi $5,89 \cdot 10^4 \text{ N/m}^2$ (yoki 422,2 mm sim. ust.) ga teng.
48. 1,14 g qalay metali 100 g simobda erib hosil qilgan amalgama eritmasi ustidagi simob bug' bosimi 754,1 mm sim. ustuniga teng. Shu haroratdagi toza simobning bug' bosimini aniqlang.
49. 500 g suvda 0,01 mol uchuvchan bo'lmagan modda erigan. Bug' bosimining nisbiy kamayishini aniqlang.
50. Eritmaning bug' bosimi toza suvning bug' bosimidan 1% past bo'lishi uchun glitserin ($\text{C}_3\text{H}_8\text{O}_3$)ning suvdagi eritmasi konsentratsiyasi qancha foiz bo'lishi kerak?
51. 100°C da suvda 5% qand ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) eriganda eritmaning bug' bosimi qanchaga teng bo'ladi? Eritmaning bug' bosimi 5% li qand eritmasinikiga teng bo'lishi uchun glitserinning suvli eritmasida necha foiz glitserin erishi kerak?
52. Simob bug' bosimi 709,9 mm sim. ust.dan 700 mm sim. ust.gacha pasayishi uchun 50 g simobda qancha qalay erishi kerak?
53. Eritma — $0,5^{\circ}\text{C}$ gacha muzlamasligi uchun 1 kg suvga necha gramm glitserin qo'shish kerak? Suvning krioskopik konstantasi 1,86.
54. Suvli eritma 0,5% mochevina ($\text{NH}_2)_2\text{CO}$ va 1% glukoza $\text{C}_6\text{H}_{12}\text{O}_6$ dan iborat. Agar suvning krioskopik konstantasi 1,86 bo'lsa, eritmaning muzlash harorati nechaga teng?
55. Suv va benzol uchun krioskopik konstantani hisoblang. Bularning suyuqlanish haroratlari 0° va $5,5^{\circ}\text{C}$ bo'lib, solishtirma suyuqlanish issiqligi mos ravishda 332 kJ/kg va 125 kJ/kg ga teng.

56. Benzol $5,42^{\circ}\text{C}$ da muzlaydi. 1000 g benzolda 12,8 g naftalin erigan eritma $4,91^{\circ}\text{C}$ da muzlaydi. Benzol $80,1^{\circ}\text{C}$ da qaynaydi. Shu qaynash haroratidagi uning bug'lanish issiqligi $95,46 \text{ kal/g}$. Shunga ko'ra:

a) bu eritmaning qaynash harorati nechaga teng?

b) $80,1^{\circ}\text{C}$ da shu eritmadagi benzolning bug' miqdori qanchaga teng?

57. Tarkibida 0,0032 mol miqdorda mochevina bo'lgan suvli eritmaning muzlash haroratini toping. Suvning suyuqlanish issiqligi $333,1 \text{ J/g}$.

58. Fenolning suyuqlanish harorati 40°C . 12,54 g fenolda 0,172 g asetanilid ($\text{C}_8\text{H}_9\text{ON}$) ning erishidan hosil bo'lgan eritma $39,25^{\circ}\text{C}$ da muzlaydi. Fenolning suyuqlanish issiqligini aniqlang.

59. Toza holdagi kadmiy 321°C da va tarkibida 10% vismuti bor kadmiy eritmasi 312°C da qotadi. Kadmiyning atom suyuqlanish issiqligini toping.

60. Toza benzolning muzlash harorati $278,5 \text{ K}$. Tarkibida $0,2242 \cdot 10^{-3} \text{ kg}$ ($0,2242 \text{ g}$) kamforasi bor $3,055 \cdot 10^{-2} \text{ kg}$ ($30,55 \text{ g}$) benzol eritmasining muzlash harorati $278,254 \text{ K}$ ga teng. Benzolning qotish harorati molal pasayishi 5,16. Kamforaning molekular og'irligini hisoblang.

61. Tekshirish uchun olingan sirka kislotasi $16,4^{\circ}\text{C}$ da muzlaydi. Amalda toza sirka kislotasi $16,7^{\circ}\text{C}$ da muzlaydi. Uning krioskopik konstantasi 3,9. 1000 g sirka kislotasi tarkibida qancha mol qo'shimcha borligini toping.

62. Eritma muzlash haroratini $0,1^{\circ}\text{C}$ ga pasaytirish uchun 1000 g suvda qancha glitserin ($M = 92$) eritish kerak? Suvning krioskopik konstantasi 1,85.

63. Shakarning suyultirilgan suvli eritmasi $272,17 \text{ K}$ da muzlaydi. Shu haroratda toza suvning bug' bosimi $568,6 \text{ N/m}^2$ ($4,255 \text{ mm sim. ust.}$), muzning suyuqlanish issiqligi $602,9 \cdot 10^4 \text{ J/kmol}$ (1440 kal/mol) ga teng. Eritmaning bug' bosimini hisoblang.

64. Suvli eritma $271,5 \text{ K}$ da muzlaydi. Uning qaynash harorati va 298 K dagi bosimini toping. Suvning krioskopik konstantasi

1,86, ebullioskopik konstantasi 0,516 ga, suv bug‘ining 298 K dagi bosimi 3168 N/m² (23,76 mm sim. ust.) ga teng.

65. 0,1 kg (100 g) suvda $2,6152 \cdot 10^{-3}$ kg (2,6152 g) etilenglikol efiri erigan eritma muzlash harorati suvning muzlash haroratidan 0,5535°C ga past. Suvning suyuqlanish issiqligi $6029 \cdot 10^{-3}$ J/kmol (1440 kmol) bo‘lsa, efirning molekular og‘irligini toping.

66. Glukoza (C₆H₁₂O₆)ning 8% li suvli eritmasi kristallanish haroratini hisoblang. Bunda 0°C da muzning suyuqlanish issiqligi 332 kJ/kg ga teng.

67. Mochevinaning suyuqlanish harorati 132,1°C, krioskopik konstantasi 21,5, sirka kislotaniki esa 16,65°C, krioskopik konstantasi 3,9 ga teng. Bu moddalarning suyuqlanish entalpiyalarini toping.

68. 20 g timolga HOC₆H₃(CH₃) C₃H₇ 0,5 g qahrabo (yantar) anhidridi (CH₂CO)₂O qo‘shilganligi sababli timolning suyuqlanish harorati 321,2 K dan 319 K gacha pasaygan. Timolning suyuqlanish entalpiyasini hisoblang.

69. Benzol 80,1°C da qaynaydi. Uning mol bug‘lanish issiqligi 30,77 kJ/mol. Tarkibida 0,01 molar qismi uchuvchan bo‘lmagan moddasi bor benzol eritmasining qaynash haroratini toping.

70. Uglerod (IV) sulfid (CS₂) 46,20°C da qaynaydi. Uning ebullioskopik konstantasi 2,3. 50 g CS₂ da 0,9373 g benzoy kislotasi eritilgan. Hosil bo‘lgan eritma 46,39°C da qaynaydi. CS₂ da erigan benzoy kislotaning molekular og‘irligini hisoblang.

71. Suvning ebullioskopik konstantasi 0,512. 5% li shakar (C₁₂H₂₂O₁₁) eritmasining qaynash haroratini aniqlang.

72. Xloroform 60,2°C da qaynaydi. Shu haroratda u uning bug‘ bosimi 781 mm sim. ust. ga teng. 1000 g xloroformda 0,2 mol uchuvchan bo‘lmagan modda erishidan hosil bo‘lgan eritmaning bug‘ bosimi va qaynash haroratini toping. Xloroformning molar bug‘lanish issiqligi 31,64 kJ/mol.

73. 68,4 g shakar (molekular og‘irligi 342) 1000 g suvda eritilgan. 100°C da eritmaning bug‘ bosimi qanchaga teng bo‘ladi?

Suvning qaynash haroratidagi bug‘lanish issiqligi 539 kal/g ga teng. Eritmaning qaynash haroratini hisoblang.

74. Etil spirti 351,4 K da va uning 0,5 molal eritmasi 352 K da qaynaydi. Etil spirtining bug‘lanish issiqligini toping.

75. Og‘irligi 0,0106 kg (10,6 g) bo‘lgan etil spirti eritmasida $0,40 \cdot 10^{-3}$ kg (0,401 g) salitsil kislota bor. Bu eritma toza spirtga nisbatan 0,337° yuqorida qaynaydi. Etil spirti qaynash haroratining molar oshishi 1,19 ga teng. Salitsil kislolaning molekular og‘irligini hisoblang.

76. Toza suv 1 atm bosimda 372,4 K da qaynaydi. Tarkibida $3,291 \cdot 10^{-3}$ kg (3,291 g) CaCl_2 va 0,1 kg (100 g) suv bo‘lgan eritmaning qaynash haroratini toping. CaCl_2 ning dissotsilanish darajasi 68%. Suvning ebullioskopik konstantasi 0,516.

77. Uchuvchan bo‘lmagan 5 g modda 25 g CCl_4 da eritilgan. Hosil bo‘lgan eritma 81,5°C da qaynaydi. Toza CCl_4 76,8°C da qaynaydi, ebullioskopik konstantasi 5,02. Eritmada erigan moddaning molekular massasini toping.

78. Sof uglerod sulfid (CS_2) 46,2°C da qaynaydi. Tarkibida 0,217 g oltingugurt va 19,18 g CS_2 bo‘lgan eritma 46,304°C da qaynaydi. CS_2 ning ebullioskopik konstantasi 2,37. CS_2 da erigan oltingugurt molekulasida qancha atom mavjud? Oltingugurtning atom massasi 32 ga teng.

79. Molekular massasi 182 bo‘lgan 0,5 g uchuvchan bo‘lmagan modda 42 g benzolda erigan. Bu eritmaning qaynash harorati 80,217°C. Toza benzolning qaynash harorati 80,1°C. Benzolning bug‘lanish issiqligini hisoblang.

80. Og‘irligi 1,2324 g naftalin 88,26 g etil efirda eritilsa, efirning qaynash harorati 0,234°C ga ortadi. Toza efirning qaynash harorati 34,0°C. Efirning bug‘lanish issiqligini toping.

81. Suyuq SO_2 10°C da qaynaydi. Uning shu haroratdagi bug‘lanish issiqligi 25,52 kJ/mol. 20 mol SO_2 da 1 mol SO_3 bo‘lgan eritmaning qaynash haroratini aniqlang.

82. Og‘irligi 0,6 g modda 25 g suvda eritilsa, eritmaning qaynash harorati 0,204°C ga, agar 0,3 g shunday modda 20 g benzolda

critilsa, qaynash harorati $0,668^{\circ}\text{C}$ ga ortadi. Suvning ebulioskopik konstantasi 0,51. Benzolning ebulioskopik konstantasini toping.

83. Gaz holdagi HBr 303 K da benzolda quyidagicha criydi:

Mol miqdor	0,000612	0,0055	0,0115	0,2535	0,02913	0,04713
Bosim (P), N/m^2	1016,3	8460,6	25771,0	39053,8	46832,4	75537,8
P , atm	0,0100	0,0835	0,2540	0,3953	0,4622	0,7455

Bosim va HBr eruvchanligining o'zaro bog'liq ravishda o'zgarishi grafigini chizing va Genri tenglamasidagi konstantaning o'rtacha qiymatini toping.

84. 300 mm sim. ustuni va 25°C da kislorodning suvda eruvchanligi 16 mg/l. 1 l eritmaga nisbatan eruvchanlikni mol da, bosimni atm. da ifoda etib, Genri konstantasini toping.

85. 1 atm. bosim va 18°C da 1 l suvda 1 l CO_2 criydi. 18°C da CO_2 bosimi 150 mm sim. ust.ga teng bo'lgan critma molar konsentratsiyasini hisoblang.

86. Umumiy bosimi 1 atm. bo'lganida 100 g suvda xlorning eruvchanligi ma'lum.

Raul qonuni bo'yicha suv bug'ining parsial bosimi va xlor bosimi 1 atm. bo'lganda uning 1000 g suvda erishini (Genri qonuniga binoan), (mol miqdori) toping.

87. CO_2 ning 25°C va $5,065 \cdot 10^5 \text{ N/m}^2$ bosimda suvda eruvchanligini hisoblang. Genri konstantasi (CO_2 uchun) $7,492 \cdot 10^{-3} \text{ N} \cdot \text{mol}$.

88. Azotning $1,013 \cdot 10^5 \text{ N/m}^2$ va $T = 20^{\circ}\text{C}$ dagi ideal eruvchanligini hisoblang. Bunda normal qaynash harorati $195,8^{\circ}\text{C}$, $\Delta H_{\text{bug.}} = 5577,3 \text{ J/mol}$.

89. 20°C da va $P_{\text{SO}_2} = 1,013 \cdot 10^5 \text{ N/m}^2$ da 65% li sulfat kislota eritmasida SO_2 ning eruvchanligi 3,55 g/100 g H_2SO_4 ga teng. Zichligi 1,56 bo'lgan 65% li sulfat kislota eritmasida erigan SO_2 ning hajmini aniqlang.

90. 20°C da va 700 mm sim. ust.da 100 ml suvda $3,54 \text{ sm}^3 \text{ CH}_4$ criydi. CH_4 ning eruvchanlik koeffitsiyentini toping.

91. 100% li SO_2 ning dizel moyida 10°C dagi eruvchanligi 40,6 g/l, 20°C da 23,4 g/l ni tashkil etadi. Eruvchanlikning molar issiqligini toping.

92. 100 g suvda 0°C da sut kislotasining eruvchanligi 2,35 g ga, $24,8^{\circ}\text{C}$ da esa 6,76 g ga teng. Kislotaning suvda erish issiqligini aniqlang.

93. CO_2 ning 20°C da suvda eruvchanligi $0,878 \text{ sm}^3/\text{ml}$, 30°C da esa $0,665 \text{ sm}^3/\text{ml}$. Eruvchanlik ideal holatda boradi deb hisoblab, CO_2 ning suvda erish issiqligini hisoblang.

94. Agar 10°C da eruvchanligi 40,6 g/l bo'lsa, SO_2 ning 0°C da dizel moyidagi eruvchanligini toping. Erish issiqligi $\Delta H = -38100 \text{ J/mol}$.

95. Agar suyuq etilen bug'lari bosimi $t_1 = 0^{\circ}\text{C}$ da $P_1 = 40,82 \cdot 10^5 \text{ N/m}^2$, $t_2 = -10^{\circ}\text{C}$ da $P_2 = 32,42 \cdot 10^5 \text{ N/m}^2$ bo'lsa, 20°C da $0,001 \text{ m}^3$ benzolda qancha gramm etilen eritish mumkin? Benzolning zichligi $0,878 \text{ g/sm}^3$. Etilenning benzoldagi eritmasini ideal eritma deb qarang.

96. Metan 90,5 K suyuqlanadi va shu haroratda suyuqlanish issiqligi $70,7 \text{ J/mol}$ ga teng bo'ladi. 50 K dagi metanning suyuq azotdagi eruvchanligini toping.

97. 125,4 g suyuq vismut 9,73 g suyuq magniy bilan aralash-tirilganda 16200 J issiqlik ajralib chiqadi. Agar magniyning shu eritmadagi parsial mol erish issiqligi 34900 J/g-atom bo'lsa, vismut uchun parsial mol erish issiqligini hisoblang.

98. Tarkibida 70 mol% Si bor bo'lgan Si—Mn suyuqlanma eritmasida kremniy uchun $\Delta H_{erish} = -3800 \text{ J/g-atom}$, marganesniki $\Delta H_e = -83500 \text{ J/g-atom}$ ga teng. Shunday tarkibli eritmadan 1 kg hosil bo'lganida ajralib chiqqan issiqlikni toping.

99. SO_2 ning suv va xloroformda taqsimlanish koeffitsiyenti 0,953. 25% SO_2 ni ajratib olish uchun xloroformda SO_2 erigan 1 l eritmaga qancha miqdorda suv qo'shish kerak?

100. Limon kislotasining suv va efirda taqsimlanish koeffitsiyenti 155 ga teng. 25% kislotani efirli eritmada ajratib olish uchun 25 ml eritmaga qancha suv qo'shish kerak?

101. Eritma tarkibidagi sirka kislotasining yarmini ajratib olish uchun 100 ml suvli eritmaga qancha efir qo'shish kerak? Sirka kislotaning suv va efirda taqsimlanish koeffitsiyenti 1,87.

102. Yodning CS_2 va suvda taqsimlanish koeffitsiyenti 590. Yodning 25°C suvda erishi 0,340 g/l ga teng. 25°C da 100 ml suvli eritma 100 ml CS_2 bilan aralashtirilganda qancha miqdorda yod qoladi?

103. Tarkibida 0,1 g yod bo'lgan 0,5 l suvli eritmada 50 ml CCl_4 qo'shilganidan keyin qancha miqdorda yod ajratib olish mumkin? Yodning suv va CCl_4 da taqsimlanish koeffitsiyenti 0,012.

104. Benzoy kislotasi benzol va suvda quyidagi konsentratsiyalarda taqsimlanadi:

Suvda	0,0150	0,0195	0,0289
Benzolda	0,242	0,412	0,970

Benzoy kislotasining taqsimlanish koeffitsiyentini hisoblang.

105. Sirka kislotasi suv (1) va CCl_4 (2) da (25°C da) quyidagicha taqsimlanadi:

C_1 , g-ekv/l	0,684	1,691	9,346
C_2 , g-ekv/l	0,015	0,0525	1,0461

CH_3COOH ning taqsimlanish koeffitsiyentini toping.

106. Fenol suv va benzolda quyidagicha taqsimlanadi:

Suvda, mol/l	0,101	0,366	0,520
Benzolda, mol/l	0,279	2,978	6,487

Fenolning taqsimlanish koeffitsiyentini hisoblang.

107. Dimetilamin suv (1) va benzolda (2) quyidagicha taqsimlanadi:

C_1 , g/mol	0,0726	0,1979	0,2652
C_2 , g/mol	0,0653	0,1877	0,2501

Dimetilaminning taqsimlanish koeffitsiyenti o'rtacha qiymatini hisoblang.

108. Anilin 25°C da suv va toluolda quyidagicha taqsimlanadi:

Suvda, mol/l	23,2	48,4	102,0
Benzolda, mol/l	181	413	1006

Anilinning suv va toluolda taqsimlanish koeffitsiyentini toping.

109. Hajmi 2 l bo'lgan suv bilan 10 g/l yodi bor 0,5 l amil spirti chayqatilganida suvga o'tgan yodning konsentratsiyasi (mol/l) nechaga teng bo'ladi? Yodning 25°C da suv va amil spirti orasidagi taqsimlanish koeffitsiyenti 230.

110. Tarkibida 0,658 g/l fenoli bor suvli eritma (25°C da) tarkibida 10,53 g/l fenoli bor amil spirti eritmasi bilan muvozanatda turibdi. 0,5 M 0,5 l suvli eritma 2 marta ekstraksiya qilinganida fenolning qancha qismi ajratib olinadi? (Har bir ekstraksiya uchun 0,1 l amil spirti olinadi).

111. Moy kislotasining suv va amil spirtida taqsimlanish koeffitsiyenti $K = 0,09$. Kislotaning suvli eritmadagi dastlabki konsentratsiyasi 0,05 kmol/m³. Eritma konsentratsiyasi 0,012 kmol/m³ bo'lishi uchun 1 m³ dastlabki suvli eritma qancha hajmdagi amil spirti bilan aralashtirilishi zarur?

112. Etil spirtining suvli eritmasi ustidagi bug'ni ideal gaz deb qabul qilib, quyidagi qiymatlar bo'yicha etil spirtining termodinamik aktivligini toping:

Eritma harorati, K	Spirit konsentratsiyasi, mol%	Spirit bug'i bosimi, mm sim.ust.
293	40	20,7
	60	25,6
	80	31,2
	100	43,6
313	40	62,5
	60	74,8
	80	91,8
	100	134
348	40	305
	60	365
	80	454
	100	667

113. Suvli eritmadagi uchuvchan bo'lmagan modda molar qismi 0,07 g ga teng. Toza suvning to'yingan bug' bosimi $32,17 \cdot 10^2$ Pa, eritma ustidagi bug' bosimi esa $26,17 \cdot 10^2$ Pa. 298 K dagi suvning aktivlik koeffitsiyentini toping.

114. 150°C da 1 mol NH_3 ning bosimi 40 atm bo'lganda 0,7696 hajmni egallaydi. Shu sharoitda NH_3 ning uchuvchanligini toping.

115. 382 K da ftorbenzolning bug' bosimi 1,974 atm ga teng. Bug'ning molar hajmi 15 l. Ftorbenzol bug'ining uchuvchanligini hisoblang.

116. 0°C da 200 atm. bosimda kislorodning uchuvchanligi 174. Kislorodning molar hajmini aniqlang.

117. 0°C da 1 mol azotning PV ko'paytmasining bosim bo'yicha o'zgarishi quyidagicha:

P , atm	1	100	200	500
PV , l·atm	22,41	22,21	23,24	31,15

Azotning 400 atm. dagi uchuvchanligini hisoblang va qaysi bosimda $f = P$ bo'lishini toping.

118. 100°C da eritmadagi suv bug'i bosimi aktivligi nechaga teng?

119. Mol konsentratsiyasi 0,8 bo'lgan shakarning suvli eritmasi $-1,6^{\circ}\text{C}$ da muzlaydi. Suvning krioskopik konstantasi 1,86. Eritmadagi shakarning aktivlik koeffitsiyentini aniqlang.

120. CS_2 da erigan aseton bug'i bosimi bilan uning molar qismi orasida quyidagicha bog'lanish bor:

N_2	0,030	0,075	0,170	0,330	0,550
P_2 , mm sim.ust.	62	120	180	217	250

Asetonning har bir eritmadagi aktivligi va aktivlik koeffitsiyentini toping.

121. Eritma ustidagi aseton bug'i bosimi 56°C da 710 mm sim. ust.ga teng. Asetonning aktivligini aniqlang.

122. Konsentratsiyasi 5 M bo'lgan glitserin eritmasi $-10,58^{\circ}\text{C}$ da muzlaydi. Suvning krioskopik konstantasi 1,86. Glitserinning aktivligini toping.

123. 273 K da suv bug'i bosimi $610,48 \text{ N/m}^2$ ($4,58 \text{ mm}$ sim. ust.), konsentratsiyasi 10% bo'lgan NaNO_3 eritmasida $P = 589,28 \text{ N/m}^2$ ($4,42 \text{ mm}$ sim ust). Suvning shu eritmadagi aktivligini aniqlang.

124. Uglerod sulfid (CS_2) da erigan metilizobutylketon bug'i bosimi bilan uning molar qismi orasida quyidagicha bog'liqlik bor:

N_2	0,040	0,070	0,180	0,350	0,650
P_2 , mm sim.ust.	65	130	205	220	280

Har qaysi eritmadagi metilizobutylketonning aktivligi va aktivlik koeffitsiyentini toping.

125. Aseton bug'i bosimi 35°C da $344,5 \text{ mm}$ sim. ust. ga, xloroformniki esa $293,1 \text{ mm}$ sim. ust.ga teng. Tarkibida 36% (molar miqdorda) xloroform bor eritma ustidagi bu komponentlarining parsial bug' bosimlari mos holda $200,8$ va $72,3 \text{ mm}$ sim. ust.ga tengdir. Shu komponentlarning eritmadagi aktivligi va aktivlik koeffitsiyentlarini toping.

KO'P VARIANTLI MASALALAR

1. Suvli eritmaning molar, molal, normal konsentratsiyalari va molar qismini hisoblang.

Variantlar	Erigan modda	Berilgan konsentratsiya, %	Eritmaning zichligi, g/ml	$T^{\circ}\text{C}$
1	AgNO_3	40	1,668	18
2	AlCl_3	30	1,242	18
3	$\text{Al}_2(\text{SO}_4)_3$	20	1,226	20
4	BaCl_2	10	1,092	20
5	BeCl_2	14	1,095	18
6	CaBr_2	25	1,250	20
7	CaCl_2	50	1,282	25
8	$\text{Ca}(\text{NO}_3)_2$	30	1,259	18

2. *A* va *B* moddalardan hosil bo'lgan eritmaning molar qismi, molar, molal va normal konsentratsiyalarini aniqlang.

Variantlar	<i>A</i> modda konsentratsiyasi, %	Moddalar		T, K	Eritmaning zichligi (10^3 kg/m^3)
		<i>A</i>	<i>B</i>		
1	2	3	4	5	6
1	97	CBr_3CHO	H_2O	323	2,628
2	94	CBr_3CHO	H_2O	313	2,566
3	91	CBr_3CHO	H_2O	313	2,485
4	87	CBr_3CHO	H_2O	313	2,340
5	80	CBr_3CHO	H_2O	313	2,106
6	73	CBr_3CHO	H_2O	313	1,938
7	63	CBr_3CHO	H_2O	313	1,725
8	45	CBr_3CHO	H_2O	313	1,476

1	2	3	4	5	6
9	72	$C_6H_5(SO_3H)$	H_2O	298	1,281
10	66	$C_6H_5(SO_3H)$	H_2O	298	1,256
11	61	$C_6H_5(SO_3H)$	H_2O	298	1,235
12	80	$C_6H_3(OH)_3$	H_2O	293	1,208
13	62	$(CH_2)_4O_2$	H_2O	293	1,041
14	57	$C_{10}H_8$	CH_3COCH_3	293	0,992
15	50	$C_{10}H_8$	CH_3COCH_3	293	0,968
16	43	$C_{10}H_8$	CH_3COCH_3	293	0,945
17	80	C_6H_{14}	CH_3COCH_3	293	0,765
18	60	C_6H_{14}	CH_3COCH_3	293	0,741
19	40	C_6H_{14}	CH_3COCH_3	293	0,719
20	20	C_6H_{14}	CH_3COCH_3	293	0,692

3. Suvli eritmaning molar qismi, foiz, molal va normal konsentratsiyalarini toping.

Variant-lar	Eritgan modda	Berilgan konsentratsiya, mol/l	Eritmaning zichligi, g/ml	$T^{\circ}C$
1	$AgNO_3$	1,405	1,194	20
2	$AlCl_3$	1,185	1,129	18
3	$BaCl_2$	1,444	1,253	20
4	$CaCl_2$	1,190	1,101	20
5	$Ca(NO_3)_2$	1,100	1,128	18
6	$CdSO_4$	1,034	1,198	18
7	$FeCl_3$	1,900	1,234	20
8	$BaSO_4$	1,150	1,205	20
9	KCl	1,500	1,120	18
10	$MnSO_4$	1,850	1,225	20

4. Suvli eritma tarkibini molar qism, foiz, molar va normal konsentratsiyalarda ifodalang.

Variant-lar	Erigan modda	Berilgan konsentratsiya, mol/1000 g	Eritmaning zichligi, g/ml	$T^{\circ}\text{C}$
1	$\text{Cu}(\text{NO}_3)_2$	1,33	1,189	20
2	CuCl_2	1,86	1,205	20
3	FeCl_2	1,97	1,200	18
4	CuSO_4	1,37	1,206	20
5	FeSO_4	1,65	1,213	18
6	KNO_3	1,55	1,135	20
7	NaNO_3	1,30	1,120	20
8	$\text{Al}(\text{NO}_3)_3$	1,44	1,165	18

5. Suvli eritmaning tarkibini foiz, molar, molal va normal konsentratsiyalarda ifodalang:

Variant-lar	Erigan modda	Berilgan konsentratsiya, molar qism	Eritma zichligi, g/ml	$T^{\circ}\text{C}$
1	HCl	0,05	1,05	20
2	HBr	0,25	1,679	20
3	AlCl_3	0,083	1,341	15
4	CaBr_2	0,083	1,635	20
5	CaCl_2	0,10	1,396	20
6	BaCl_2	0,20	1,285	20

6. Talliy (2) — simob (1) aralashmasidan hosil bo'lgan 1 kg eritmaning 298 K parsial mol entalpiyasi ($\Delta\bar{H}$), entalpiya o'zgarishi (ΔH_1), entropiyasi (ΔS) va izobarik-izotermik potensialini (ΔG) quyidagi berilganlar asosida toping (N_2 talliyning atom qismi).

Variant-lar	N_2	$\Delta\bar{G}_1$, J/mol	$\Delta\bar{G}_2$, J/mol	$\Delta\bar{S}_1$, J/mol · grad	$\Delta\bar{S}_2$, J/mol · grad
1	2	3	4	5	6
1	0,010	-12,97	-14042	0,04	29,25
2	0,055	-182,8	-11000	0,29	28,01
3	0,085	-305,4	-6862	0,63	17,36
4	0,150	-610,9	-4389	1,26	12,05
5	0,200	-849,4	-3163	1,67	10,17
6	0,250	-1130	-2171	2,34	7,70
7	0,290	-1343	-1619	2,97	6,07
8	0,360	-1711	-820,1	3,43	5,02
9	0,405	-1975	-355,6	4,14	3,85
10	0,455	-2144	-264,2	6,05	2,28

7. A moddadan $b\%$ li $\begin{cases} a \text{ kg miqdori} \\ c \text{ kg suv bilan} \end{cases}$ 298 K da suyultirilganda

ajralib chiqadigan yoki yutiladigan issiqlikni aniqlang. Hisoblashlar uchun ilovada keltirilgan ma'lumotnoma bo'yicha integral erish issiqliklari qiymatlaridan foydalaning.

Variant-lar	A modda	a	b	c	Variant-lar	A modda	a	b	c
1	HCl	1	26	2	11	NaOH	2	35	4
2	HCl	2	38	3	12	KOH	3	50	2
3	HCl	3	30	4	13	KOH	4	45	3
4	H ₂ SO ₄	4	90	1	14	KOH	5	40	1
5	H ₂ SO ₄	5	80	2	15	HNO ₃	2	50	4
6	H ₂ SO ₄	1	70	3	16	HNO ₃	3	40	5
7	H ₂ SO ₄	2	60	3	17	HNO ₃	4	30	10
8	NaOH	3	30	1	18	LiCl	5	30	3
9	NaOH	4	25	2	19	NaBr	2	40	6
10	NaOH	5	40	3	20	NaCl	4	26	10
					21	NaJ	5	30	10

8. T haroratda c konsentratsiyali uchuvchan bo'lmagan modda suyuq erituvchida eriganda hosil bo'lgan eritma bug' bosimi P (Pa) ga, zichligi d ga teng. Suyuq va qattiq holdagi toza erituvchining to'yingan bug' bosimi haroratga bog'liqligidan (jadvalda keltirilgan) foydalanib quyidagilarni aniqlang:

- 1) erigan moddaning molekular massasi;
- 2) eritmaning molar va molal konsentratsiyasi;
- 3) osmotik bosimi;
- 4) ebullioskopik konstantasi;
- 5) eritma muzlash haroratining pasayishi;
- 6) krioskopik konstantasi.

Variant-lar	Uchuvchan modda miqdori	Erituvchining molekular massasi	P, Pa	$T \text{ K}$	Zichlik kg/m^3
1	0,5	18	1547	288	1,000
2	8	27	34058	278	0,750
3	5	28	31740	69	0,850
4	8,5	30	33841	114	1,300
5	5	32	16108	306,7	1,590
6	9	34	55000	207	1,985
7	8	44	650000	223	1,500
8	7	46	2375	282	1,210
9	5	52	95042	252,5	2,900
10	4,5	52,5	645	1990	6,800
11	5	58	39982	300	3,560
12	6	64	7328	218	1,590
13	3	68	12420	149	1,780
14	3	78	4627	280	0,750
15	6	81	51852	195	1,210
16	5	83,5	84990	119,6	2,160

9. Gazlarning turli haroratda va umumiy bosim (gaz va suv bug'i uchun) $1,01 \cdot 10^5 \text{ Pa}$ da suvda eruvchanligi qiymatlaridan foydalanib (jadvalda keltirilgan), ularning suvda o'rtacha erish issiqligini toping.

Variant-lar	Gaz nomi	Gazning T da suvda eruvchanligi, g/100 g · H ₂ O							
		273	283	293	303	313	323	333	353
1	Azot	2,94	2,31	1,89	1,62	1,39	1,21	1,05	0,66
2	Azot (II) oksidi	9,83	7,56	6,17	5,17	4,39	3,76	3,24	1,98
3	Asetilen	0,200	0,150	0,117	0,094	—	—	—	—
4	Vodorod	1,92	1,74	1,60	1,47	1,39	1,29	1,18	0,79
5	Geliy	—	1,75	1,74	1,72	1,70	1,69	—	—
6	Kislorod	6,95	5,37	4,34	3,59	3,09	2,66	2,27	1,38
7	Metan	3,95	2,96	2,32	1,90	1,59	1,36	1,14	0,695
8	Oltinugurt dioksidi	22,8	16,2	11,3	7,80	5,41	—	—	—
9	Vodorod sulfid	0,707	0,511	0,385	0,298	0,236	0,188	0,148	0,077
10	Uglerod dioksidi	0,335	0,232	0,169	0,125	0,097	0,076	0,058	—
11	Uglerod oksidi	4,40	3,48	2,84	2,41	2,08	1,80	1,52	0,98
12	Xlor	2,46	0,997	0,730	0,572	0,459	0,393	0,329	0,223
13	Vodorod xlorid	82,5	77,2	72,1	67,3	63,3	59,6	56,1	—
14	Etan	1,32	0,87	0,62	0,47	0,37	0,30	0,24	0,13
15	Etilen	0,0284	0,0200	0,149	0,0148	—	—	—	—

VII bob

FAZALAR MUVOZANATI

VII.1. FAZALAR QOIDASI

Agar sistema geterogen bo'lib, bir qancha ayrim qismlardan iborat bo'lsa, sistemani o'rganishda uch narsani aniqlash kerak bo'ladi: 1) qismlarning soni; 2) ularning tarkibi; 3) termodinamik xossasi. Sistema qismlari sonini — fazalar soni (f), tarkibini — komponentlar soni (K) va termodinamik xossasini — erkinlik darajalar soni (C) ifoda qiladi.

Faza deb sistemaning boshqa qismlaridan ko'zga ko'rinadigan sirt yuzasi bilan ajralgan qismiga aytiladi. Komponentlar soni sistema tarkibini aniqlash uchun kifoya bo'lgan tarkibiy qismlarning eng kichik soni. U sistemani tashkil qilgan moddalar soni bilan ular o'rtasidagi mavjud reaksiyalar soni farqiga teng bo'ladi. **Erkinlik darajalar soni** — termodinamik xossalarini (T , V , P) aniqlash uchun kerak bo'lgan parametrlarning eng kichik soniga teng.

Bu uch kattalik bir-biri bilan quyidagicha bog'langan:

$$f + C = K + 2 . \quad (\text{VII.1})$$

Bu tenglama Gibbsning fazalar qoidasining matematik ifodasidir.

VII. 2. BIR KOMPONENTLI SISTEMALAR

Toza moddalarning bir agregat holatdan boshqa agregat holatga o'tishi, qattiq moddalarning allotropik o'tishlaridagi jarayonni Klauzius-Klayperon tenglamasi ifoda qiladi:

$$\Delta H = T \frac{dP}{dT} (V_2 - V_1), \quad (\text{VII. 2})$$

bunda: V_2 , V_1 — yuqori va pastki haroratdagi hajmlar: $(V_s - V_q)$, $(V_g - V_s)$, $(V_g - V_q)$; ΔH — yashirin o'tish issiqlik effekti;

T — o'tish harorati; $\frac{dP}{dT}$ — bug' bosimining harorat bilan o'zgarishi.

Solishtirma hajm (1 gramm massa hajmi) kabi ΔH — solishtirma issiqlik effekti bo‘ladi. Agar hajmlar molar hajm bo‘lsa, ΔH — molar yashirin issiqlik effekti bo‘lib, J/mol bo‘ladi. $\frac{dP}{dT}$ qiymati ($V_2 - V_1$) alohidi bilan belgilanadi va hamma moddalarda $V_2 > V_1$ (suv bundan mustasno, unda $V_1 > V_2$) hamda $\frac{dP}{dT} > 0$.

Demak, bu kattaliklar proporsional (mutanosib) ravishda o‘zgaradi. $\frac{dT}{dP}$ esa bosim o‘zgarishi bilan haroratning o‘zgarishini ko‘rsatadi.

Suyuqliklarning bug‘lanish jarayonida bug‘ hajmi suyuqlik hajmiga nisbatan juda ko‘p marta katta ($V_g \gg V_n$) bo‘lganligidan suyuqlik hajmini bug‘ hajmiga nisbatan e‘tiborga olmasa ham bo‘ladi, ya’ni $V_g - V_n = V_g$, unda (VII.2) tenglamadan:

$$\Delta H = T \frac{dP}{dT} V, \quad (\text{VII.3})$$

bunda: V — bug‘ hajmi. Agar bug‘ ideal gazlar qonuniga bo‘ysunadi deb faraz qilinsa; $V = \frac{RT}{P}$, unda (VII. 3) tenglama

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT; \quad d \ln P = \frac{\Delta H}{RT^2} dT \quad \text{va} \quad \lg P = -\frac{\Delta H}{2,3 \cdot RT} + \text{const} \quad (\text{VII.4})$$

yoki T_1 va T_2 haroratda ($T_2 > T_1$):

$$\lg \frac{P_2}{P_1} = \frac{\Delta H}{2,3R} \cdot \frac{T_2 - T_1}{T_1 \cdot T_2}. \quad (\text{VII. 5})$$

Fazoviy aylanishda (allotropik aylanishda) fazoviy issiqlik effekti ΔH_f harorat bilan quyidagicha bog‘lanadi:

$$-\frac{d(\Delta H_f)}{dT} = \Delta C_p = C^\alpha - C^\beta. \quad (\text{VII.6})$$

C^α , C^β lar muvozanatda turgan α va β fazalarning issiqlik sig‘imi. Kichik harorat oralig‘ida $\Delta C = \text{const}$ deb qabul qilish mumkin. Bu holda:

$$\Delta H_{f,T} = \Delta H_0 + \Delta C_f T \quad (\text{VII.7})$$

yoki

$$\Delta H_{f,T_2} = \Delta H_{f,T_1} + \Delta C_f (T_2 - T_1). \quad (\text{VII.7}^1)$$

Yuqoridagi suyuqlanish, ya'ni «suyuqlik — bug'» fazalar muvozanati uchun mansub tenglamalarni sublimatsiya, ya'ni «qattiqlik — bug'» fazalar muvozanati uchun ham qo'llash mumkin.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Difenilamin (C_6H_5)₂NH ning molar suyuqlanish issiqligini aniqlang. 1 kg difenilamin suyuqlanganda hajm ($V_s - V_q = \Delta V$) $9,58 \cdot 10^{-5} \text{ m}^3$ ga o'zgargan:

$$\frac{dT}{dP} = 2,67 \cdot 10^{-7} \text{ grad} \cdot \text{m}^2/N.$$

Difenilaminning suyuqlanish harorati 34°C ga, molekular massasi 169 ga teng.

Y e c h i s h . (VII.2) tenglamaga muvofiq:

$$\Delta H = T \frac{dP}{dT} \Delta V.$$

Molekulalar hajmi $\Delta V = 9,58 \cdot 10^{-5} \cdot 169 \cdot 10^{-3}$, m^3/mol bo'ladi.

$$T_{\text{suyuq.}} = 273 + 34 = 307 \text{ K}.$$

$$\Delta H = 307 \frac{9,58 \cdot 10^{-5} \cdot 169 \cdot 10^{-3}}{2,67 \cdot 10^{-7}} = 19,84 \cdot 10^3 \text{ J/mol} = 19,84 \text{ kJ/mol}.$$

2. Naftalinning suyuqlanish issiqligi $148,639 \cdot 10^3 \text{ J/kg}$ va suyuqlanish harorati $T = 353,3 \text{ K}$ ga teng. Suyuqlanishda hajm o'zgarishi $\Delta V = V_c - V_q = 0,146 \cdot 10^{-3} \text{ m}^3/\text{kg}$. Bosim 1,013310 ga o'zgariganda suyuqlanish harorati qanchaga o'zgaradi?

Y e c h i s h . (VII.2) tenglamaga muvofiq:

$$\frac{dP}{dT} = \frac{\Delta P}{\Delta T} = \frac{\Delta H}{T \Delta V} \quad \text{va}$$

$$\Delta T = \frac{\Delta P \cdot T \cdot \Delta V}{\Delta H} = \frac{0,0133 \cdot 10^5 \cdot 353 \cdot 146 \cdot 10^{-3}}{148,639 \cdot 10} = 0,0351^\circ\text{C}.$$

3. Etil spirtining solishtirma bug‘lanish issiqligi $\Delta H = 887,644 \cdot 10^3 \text{ J/kg}$; $T_1 = 343 \text{ K}$ da to‘yingan bug‘ bosimini aniqlang. Etil spirtining mol massasi 46 ga teng.

Yechish. (VII.6) tenglamadan foydalaniladi:

$$\lg \frac{P_2}{P_1} = \frac{\Delta H}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right).$$

R qiymati 1 mol moddaga nisbatan berilganligidan, bug‘lanish issiqligini ham 1 mol ga nisbatan olish kerak va demak:

$$\Delta H = 887,644 \cdot 10^3 \cdot 46 \text{ bo‘ladi.}$$

$$\begin{aligned} \lg P_2 = \lg P_1 + \frac{\Delta H}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) &= \lg 0,721 \cdot 10^5 + \frac{887,044 \cdot 10^3 \cdot 46(353 - 343)}{2,38,314 \cdot 343 \cdot 353} = \\ &= 4,8755 \quad \text{va} \quad P = 0,7509 \cdot 10^5 \text{ Pa.} \end{aligned}$$

4. Toluolning bug‘ bosimi harorat bilan quyidagicha o‘zgaradi:

$$\lg P = -\frac{2866,53}{T} - 6,71 \lg T + 20,775.$$

$T = 383,3 \text{ K}$ qaynash haroratidagi molar bug‘lanish issiqligini aniqlang.

Yechish. (VII. 4) tenglamadan:

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2} = \frac{2,3 \cdot 2866,533}{T_2} - \frac{6,71}{T}$$

$$\Delta H = 2,3R \cdot 2866,53 -$$

$$6,71 \cdot RT = 2,3 \cdot 8,314 \cdot 10^3 \cdot 12866,53 \cdot$$

$$\cdot 6,71 \cdot 8,31 \cdot 10^3 \cdot 383,3 = 33,585 \cdot 10^6, \text{ J/kmol.}$$

$$R = 8,314 \text{ J/mol} \cdot \text{grad yoki } 8,314 \cdot 10^3 \text{ J/kmol} \cdot \text{grad.}$$

5. Uglerod (IV) sulfid (CS_2) suyuqligi orqali 40°C (313 K) va 720 mm sim. ust. ga teng bosimda $0,005 \text{ m}^3$ havo o'tkazilgan. Qancha CS_2 ajratib olish mumkinligini aniqlang. Normal sharoitda CS_2 ning $46,5^\circ$ (319,5 K) qaynash haroratida bug'lanish issiqligi $355,8 \text{ J/g}$ ga teng. CS_2 ning mol massasi $M = 76$.

Yechish. Oldin CS_2 ning parsial bosimini aniqlab, so'ng Klayperon tenglamasidan foydalanib n - mol soni va gramm bilan ifodalangan miqdori aniqlanadi. (VII.5) tenglamadan foydalanib CS_2 ning 40°C dagi parsial bosimi aniqlanadi:

$$\lg \frac{P_2}{P_1} = \frac{\Delta H}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right), \text{ bundan}$$

$$\lg P_1 = \lg P_2 - \frac{\Delta H}{2,3R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \lg 760 - \frac{355,8 \cdot 76 \cdot 6,5}{2,3 \cdot 8,314 \cdot 313 \cdot 319,5} = 2,79$$

va $P_1 = 615 \text{ mm sim. ust.}$

Solishtirma bug'lanish issiqligidan molar bug'lanish issiqligiga o'tish uchun ΔH qiymati CS_2 mol massasi — 76 ga ko'paytirildi.

Havoning parsial bosimi = $720 - 615 = 105 \text{ mm sim. ust.}$ ga teng.

Boyl-Mariott tenglamasidan havo aralashmasining hajmi aniqlanadi:

$$p_1 V_1 = p_2 V_2, \text{ ya'ni } 0,005 \cdot 720 = V \cdot 105, \text{ bundan}$$

$$V = \frac{0,005 \cdot 720}{105} = 0,0343 \text{ m}^3.$$

CS_2 bug'ining miqdori Klayperon tenglamasidan foydalanib topiladi:

$$n = \frac{P_1 V}{RT} = \frac{615 \cdot 0,0343 \cdot 1,0133 \cdot 10^5}{760 \cdot 8,314 \cdot 313} = 1,16 \text{ mol},$$

$$g = 1,16 \cdot M_{\text{CS}_2} = 1,16 \cdot 76 = 88,5 \text{ g}.$$

6. Ruxning haydalish (sublimatsiya) issiqligi DH_h ni aniqlang. $697,2 \text{ K}$ da (uchlamchi nuqtada) ruxning suyuqlanish issiqligi (DH_s) $6,908 \text{ kJ/mol}$ ga teng. Bug'lanish issiqligi (DH_b) harorat bilan quyidagicha bog'langan:

$$\Delta H_b = 133738,66 - 9,972 \cdot T \text{ J/mol.}$$

Yechish. Ma'lumki:

$$\Delta H_h = \Delta H_s + \Delta H_b.$$

Tenglama shartida ΔH_s — ma'lum. Demak, ΔH_h ni aniqlash uchun uni hisoblab topish kerak bo'ladi.

Yuqoridagi bog'lanishdan ΔH_b ning $T = 692,7 \text{ K}$ dagi qiymati topiladi:

$$\Delta H_b = 133738,66 - 9,972 \cdot 692,7 = 126,825 \text{ kJ/mol;}$$

$$\Delta H_h = 126,825 + 6,908 = 133,73 \text{ kJ/mol.}$$

7. Suyuq ruxning bug' bosimi (mm sim. ust. o'lchamida) harorat bilan quyidagicha o'zgaradi:

$$\lg P = -\frac{6997}{T} - 1,2 \lg T + 12,247.$$

Ruxning suyuqlanish harorati $692,7 \text{ K}$ da ruxning bug'lanish issiqligi ΔH_b ni aniqlang.

Yechish. $692,7 \text{ K}$ da ruxning bug'lanish issiqligini aniqlash uchun (VII.4) tenglamadan foydalaniladi:

$$\Delta H_b = \left(\frac{d \ln P}{dT} \right) RT^2.$$

Demak, avvalo ruxning bug' bosimi harorat bilan o'zgarishini ifoda qilgan tenglamada $\lg$ dan $\ln$ ga o'tish kerak:

$$\ln P = -\frac{6997 \cdot 2,3}{T} - 1,2 \ln T + 12,247 \cdot 2,3.$$

Bu tenglamani differentsiallab:

$$\frac{d \ln P}{dT} = \frac{6997 \cdot 2,3}{T^2} - \frac{1,2}{T}$$

topiladi va bunga ko'ra:

$$\Delta H_b = \frac{d \ln P}{dT} RT^2 = \left(\frac{6997 \cdot 2,3}{T^2} - \frac{1,2}{T} \right) RT^2 = 6997 \cdot 2,3R - 1,2TR.$$

ΔH_b $692,7 \text{ K}$ haroratda aniqlanadi.

$$\Delta H_b = 6997,2 \cdot 2,3 \cdot 8,314 - 1,2 \cdot 8,314 \cdot 692,7 = 126,887 \text{ kJ/mol.}$$

8. 298K da α FeS ning β FeS ga o'tish fazoviy issiqlik effektini aniqlang. $T_{ayl.}$ 298 K chegarasida $\Delta C = \text{const}$ deb qabul qiling. β FeS ning o'rtacha issiqlik effekti

$$S_\beta = 53,845 \text{ J/mol}$$

$$S_\alpha = 54,85 \text{ J/mol} \cdot \text{grad}; T_{ayl.} \alpha 411 \text{ K.}$$

$$\Delta H_{f, 298} = 4396,35 \text{ J/mol.}$$

Yechish. (VII. 6) va (VII. 7) tenglamalarga muvofiq:

$$\Delta H_{f, 298} = \Delta H_{f, ayl} + \Delta S (298 - T_{ayl});$$

$$\Delta C_p = C_b - C_a = 53,84 - 54,85 = -1,005 \text{ J/mol} \cdot \text{grad.}$$

va

$$\Delta H_{f, 298} = 4396,35 - 1,005 \cdot (298 - 411) = 4509 \text{ J/mol.}$$

VII.3. IKKI KOMPONENTLI SISTEMALAR

«Suyuqlik-bug'» fazalar muvozanati

Agar bir-birida cheksiz eriydigan (aralashadigan) A va B suyuqliklardan iborat sistemalar qaynatilsa, «suyuqlik-bug'» fazalari hosil bo'lib, ma'lum harorat va bosimda muvozanatda bo'ladi. Suyuqlik va bug' fazalar tarkibi ko'pincha har xil bo'ladi. P_A° , P_B° — toza A va B moddalarning bug' bosimi, P_A , P_B — eritmadagi bug' bosimi, N_A , N_B — A va B moddalarning suyuq fazadagi va N_A^l , N_B^l — bug'dagi molar qismlari bo'lsa, ular o'rtasidagi quyidagi bog'lanishlarni (Raul qonunidan foydalanib) topish mumkin.

Suyuqlik va bug' fazasida konsentratsiyalar quyidagicha bog'langan:

$$N_A^l = \frac{P_A^\circ}{P} N_A; \quad N_B^l = \frac{P_B^\circ}{P} N_B; \quad (\text{VII.8})$$

P — eritma ustidagi bug'ning umumiy bosimi $P = P_A + P_B$:

$$\left(\frac{1}{N_A^I} - 1\right) = \frac{P_B^0}{P_A^0} \left(\frac{1}{N_A} - 1\right) \quad (\text{VII.9})$$

$$\left(\frac{1}{N_B^I} - 1\right) = \frac{P_A^0}{P_B^0} \left(\frac{1}{N_B} - 1\right). \quad (\text{VII.10})$$

(VII. 9) tenglama «tarkib—harorat» koordinatasiga qo'yilsa, ideal sistemalar uchun to'g'ri chiziqli (VII.1-rasm) va real sistemalar uchun (VII.2-rasm) holatlarni ko'rsatuvchi diagrammalar hosil qilinadi.

Bunday sistemalardagi muvozanat «tarkib—xossa» diagrammasida o'rganiladi va diagramma **holat diagrammasi** deyiladi.

t_A^0, t_B^0 nuqtalar toza A va B moddalarning qaynash harorati.

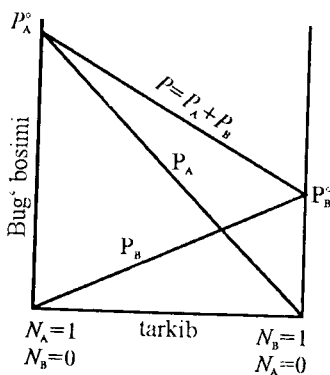
Ko'pincha absissalar o'qiga sistema tarkibi va ordinatalar o'qiga esa qaynash haroratlari qo'yiladi. Muvozanatdagi biror ma'lum haroratga ikki xil tarkib, ya'ni suyuqlik va bug' tarkiblari to'g'ri keladi. Rasmda t_A t_B chizig'i suyuqlik, t_A t_B chizig'i esa bug' tarkibini belgilovchi nuqtalar majmuidir.

t_A t_B chizig'i suyuqlik, t_A t_B esa bug' chizig'i bo'lib, suyuqlik egrisining pastida bitta faza — suyuqlik, t_A t_B chizig'i ustida faqat bug' faza va ularning o'rtasida sistema geterogen bo'lib, ikki faza — bug' va suyuqlikdan iborat.

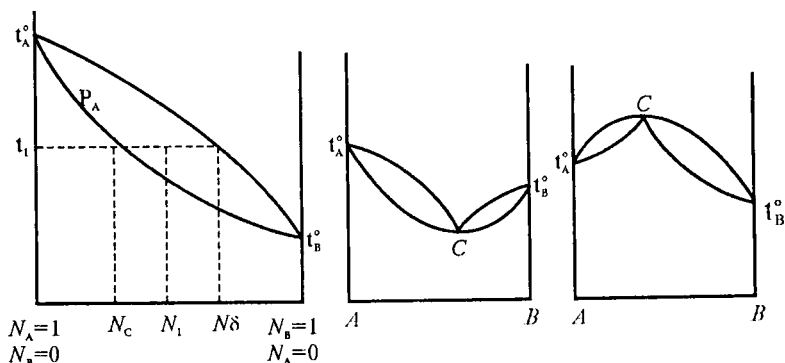
Masalan, N_1 tarkibli va t haroratga to'g'ri kelgan A nuqtadagi sistema suyuq va bug' fazalaridan iborat bo'ladi. Bu sohada suyuqlik va bug' massalar miqdori (massasi) **richag qoidasidan** foydalanib aniqlanadi, ya'ni:

$$m_b H = m_s M,$$

m_s, m_b — suyuqlik (critma) va bug' fazalar massasi, H — bug' faza yelkasi



VII. 1-rasm.
Real sistemalarning holat diagrammasi.



VII. 2-rasm. Real sistemalarning holat diagrammalari.

(bd — chiziq uzunligi) va M — eritma faza yelkasi (ad — chiziq uzunligi) bo'lsa, richag qoidasiga muvofiq:

$$\frac{m_s}{m_b} = \frac{(bd)}{(ad)}.$$

Grafikdan yelkalarni o'lchab, massasining nisbati aniqlanadi va umumiy massa $m = m_s + m_b$ ma'lum bo'lsa, bu ikki tenglamadan har qaysi fazaning ayrim massasini aniqlash mumkin.

N_s , N_b — ma'lum haroratdagi suyuqlik va bug' fazalarning tarkibini ko'rsatadi.

Ba'zi sistemalarda bug' egrisi ekstremumdan (maksimum yoki minimum) o'tadi. Ekstremum nuqtadagi eritma **azeotrop eritma** (*aralashma*) deyiladi. Azeotrop eritmada suyuqlik va bug' fazalar bir xil tarkibda bo'ladi va qaynash jarayonida suyuqlik va bug' fazalarning tarkibi o'zgarmaydi va shunga ko'ra turg'un haroratda qaynaydi. Azeotrop aralashmani haydash yo'li bilan to'la tarkibiy qismlarga ajratish mumkin emas. Toza A (yoki B) moddaning bir qismi toza holda ajraladi va bir qismi azeotrop aralashmada qoladi.

Agarda sistema bir-birida erimaydigan (aralashmaydigan) A va B suyuqliklardan iborat bo'lsa, umumiy bug' bosimi A va B larning toza holdagi bug' bosimlarining yig'indisiga teng bo'ladi:

$$P = P_A^0 + P_B^0. \quad (\text{VII. 11})$$

$P > P_A^0$ Ba $P > P_B^0$ bo'lganligidan, sistema ayrim moddalarga qaraganda past haroratda qaynaydi. Ba'zi, ayniqsa organik moddalar qarorsiz bo'lib, ular toza holda qaynatib haydalganda qaynash haroratiga bormasdan ajralib ketadi. Shunga ko'ra, bu xil moddalar suv bug'i bilan haydaladi. Bu holda bug' va kondensatning tarkibi bir xil bo'ladi:

$$m_{\text{H}_2\text{O}} = m_B \cdot 18 P_{\text{H}_2\text{O}}^0 / (M_B \cdot P_B^0). \quad (\text{VII. 12})$$

$m_{\text{H}_2\text{O}}$ esa m_B miqdordagi B moddani haydash uchun kerak bo'lgan suv miqdori, M_B — B moddaning mol massasi. 1 kg B moddani haydash uchun kerak bo'lgan suv miqdori:

$$m_{\text{H}_2\text{O}}^1 = 18 \cdot P_{\text{H}_2\text{O}}^0 (M_B \cdot P_B^0).$$

Bu yerda $m_{\text{H}_2\text{O}}$ 1 kg B moddani haydash uchun kerak bo'lgan suv — *sarf koeffitsiyenti* ham deyiladi.

MASALALAR YECHISHGA DOIR MISOLLAR

9. 132,3°C da brombenzol (1) va xlorbenzolning to'yingan bug' bosimi mos ravishda 400 va 762 mm. simob ustuniga teng. Bu moddalar bir-birida cheksiz erib, ideal eritma hosil qiladi. Quyidagilar aniqlansin: 1) 760 mm sim. bosimi ostida qaynovchi aralashmaning 132,3°C dagi tarkibi; 2) a) 1 mol% $\text{C}_6\text{H}_5\text{Cl}$ va b) 1 mol% $\text{C}_6\text{H}_5\text{Br}$ tutgan eritma ustidagi bug'ning tarkibi (mol soni hisobida); 3) turg'un haroratda haydash davomida suyuqlik tarkibi qanday o'zgaradi?

Y e c h i s h. 760 mm sim. ust. bosimida 132,3°C da qaynaydigan aralashma tarkibi (VII. 9) tenglamadan foydalanib topiladi, agar 1 — $\text{C}_6\text{H}_5\text{Br}$ va 2 — $\text{C}_6\text{H}_5\text{Cl}$ bo'lsa,

$$P = P_1^0 + N_2(P_2^0 - P_1^0) \text{ dan}$$

$$N_2 = \frac{P - P_1^0}{P_2^0 - P_1^0} = \frac{760 - 400}{762 - 400} = 0,99\%.$$

Demak,

$$N_2 = 99,4\% (\sim 99), N_1 = 100 - 99,4 = 0,6 (\sim 0,1) \text{ mol\%}.$$

2) Moddalarining bug'dagi mol nisbatini Daltonning parsial bosimlar qonunidan foydalanib aniqlaymiz:

$$\frac{n_1}{n_2} = \frac{P_1}{P_2}.$$

Demak, buning uchun parsial bosimlarni aniqlash kerak. Bunda (VII. 9) tenglamadan foydalaniladi:

$$P_1 = N_1 \cdot P_1^0 = 400 \cdot 0,99 = 396 \text{ mm sim. ust};$$

$$P_2 = N_2 \cdot P_2^0 = 762 \cdot 0,001 = 7,62 \text{ mm sim. ust};$$

$$\frac{n_1}{n_2} = \frac{7,62}{396} = 0,019.$$

Demak, brombenzol xlorbenzoldan 0,019 marta kam yoki xlorbenzol C_6H_5Br dan 51,97 marta ko'p.

3) Aralashmada 1 mol % C_6H_5Cl bo'lganda bug' fazada mol sonlari nisbatini aniqlaymiz. Buning uchun yana parsial bosimlar hisoblab topiladi:

$P_1 = 400 \cdot 0,01 = 4 \text{ mm sim. ust.}$ (N foizdan $\rightarrow$ molar qismga aylantirilganda $100\% \rightarrow 0,01$).

$$P_2 = 762 \cdot 0,99 = 754 \text{ mm sim. ust.}$$

va

$$\frac{n_1}{n_2} = \frac{754,38}{4} = 188,6.$$

Bug' fazada:

$$\frac{n_2}{n_1} = \frac{P_2}{P_1} = \frac{P_2^0 \cdot N}{P_1^0 \cdot N_1} = \frac{400 \cdot N_2}{762 \cdot N_1} = 1,905 \cdot \frac{N_2}{N_1}.$$

Demak, bug'da C_6H_5Cl ning mol soni C_6H_5Br ning mol soniga nisbatan (suyuqlikdagi nisbatga ko'ra) 1,905 marta ko'p. Shuning uchun qaynatish davom etgan sari suyuqlikda C_6H_5Br miqdori aralashmada molar qismi ko'paya boradi.

10. $T = 313$ K haroratda benzol (C_6H_6) va dixlorektan $C_2H_4Cl_2$ larning to'yingan bug' bosimi mos ravishda 20328,3 va 20661,5 Pa ga teng. Eritma 0,3 mol benzol va 0,9 mol dixlorektan iborat. Eritma bilan muvozanatda turgan bug'ning tarkibini aniqlang.

Yechish. (VII.10) tenglamaga muvofiq suyuqlik va bug' fazalar tarkibi quyidagicha bog'langan:

$$\left(\frac{1}{N_A^I} - 1\right) = \frac{P_B^0}{P_A^0} \left(\frac{1}{N_A} - 1\right).$$

N_A^I , N_A — bug' va suyuqlik fazada A moddaning molar qismi.

Agar $A = C_6H_6$ va $B = C_2H_4Cl_2$ deb belgilasak, bu tenglamani yechish uchun avvalo N_A suyuqlikdagi A moddaning molar qismini topish kerak:

$$N_A = \frac{n_A}{n_A + n_B} = \frac{0,3}{0,6 + 0,9} = \frac{0,3}{1,2} = 0,25.$$

Demak:

$$\frac{1}{N_A^I} - 1 = \frac{P_B^0}{P_A^0} \left(\frac{1}{N_A} - 1\right) = \frac{20661,5}{20328,3} \left(\frac{1}{0,25} - 1\right).$$

Agar bu tenglamadan N_A^I ni topsak:

$$\frac{1}{N_A^I} = 1 + \frac{20661,5}{20328,85} \left(\frac{1}{0,25} - 1\right) = 1 + 1,016 \cdot 3 = 4,049.$$

$$N_A^I = \frac{1}{4,049} = 0,247.$$

Demak, bug' fazada benzolning molar qismi suyuqlikdagiga qaraganda kam bo'lar ekan.

11. Mol miqdori bilan 80% $(CH_3)_2CO$ va 20% CS_2 dan iborat aralashmadan 1 kg olib haydalgan. Bu eritma 40% $(CH_3)_2CO$ va 60% CS_2 dan iborat azeotrop aralashma beradi. Shu tarkibda bug' egrisi minimumdan o'tadi (VII.3-rasm). Qaysi modda va qancha miqdorda rektifikatsiyalanib (haydash) toza holda ajraladi?

Yechish. 1 kg sistemada qancha mol CS_2 va qancha mol $(CH_3)_2CO$ borligini aniqlaymiz:

$$n_{as} \cdot M_{as} + n_{CS_2} M_{CS_2} = 100$$

$$n_1 = 4n_2$$

va bundan:

$$4n_2M_{\text{as}} + n_{\text{CS}_2}M_{\text{CS}_2} = 1000$$

$$n_{\text{CS}_2} = 3,247 \text{ mol};$$

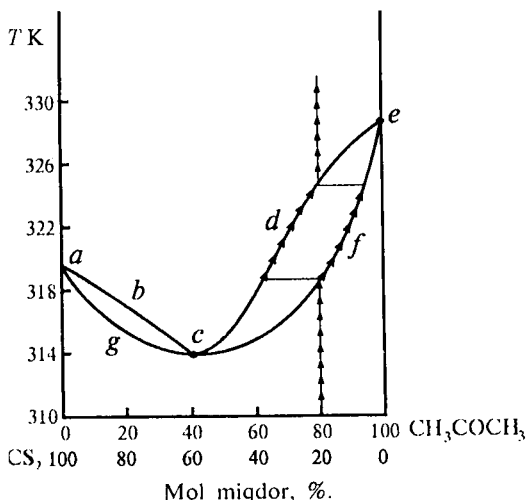
$$n_{(\text{CH}_3)_2\text{CO}} = 12,987.$$

Sistema tarkibi minimum nuqtadan o'ng tomonda bo'lganligidan toza holda faqat aseton ajraladi, CS_2 ning hammasi (3,247 mol) azeotrop aralashmada bo'ladi (azeotrop aralashmada mol hisobida CS_2 63% ni tashkil qiladi). Qolganini 37% aseton tashkil qiladi:

$$3,247 \text{ mol} - 63\%,$$

$$x - 37\%$$

$$x = \frac{3,247 \cdot 30}{63} = 1,907.$$



VII. 3-rasm.

Demak, 1,907 mol azeotropda $12,987 - 1,907 = 11,01$ mol aseton sof holda ajralib chiqadi yoki $11,01 - M_{(\text{CH}_3)_2\text{CO}} = 11,01 \cdot 58 \cdot 10^{-3} = 0,6386$ kg aseton qoladi.

12. Suv va toluol bir-birida erimaydi. Toluol suv bug'i bilan haydaladi va ularning aralashmasi 358,3 K da qaynaydi. Shu haroratda toluolning bug' bosimi $4,800 \cdot 10^4$ Pa va suvning bug' bosimi $6,200 \cdot 10^4$ Pa ga teng. 1 kg toluolni haydash uchun qancha suv kerak bo'ladi? Toluolning mol massasi $M = 92$ ga teng.

Y e c h i s h . (VII.12) tenglamaga muvofiq:

$$m_{\text{H}_2\text{O}} = 18 \cdot 6,20 \cdot 10^4 (4,800 \cdot 10^4 \cdot 92) = 0,253 \text{ kg}.$$

VII.4. «QATTIQ-SUYUQ» FAZALAR MUVOZANATI

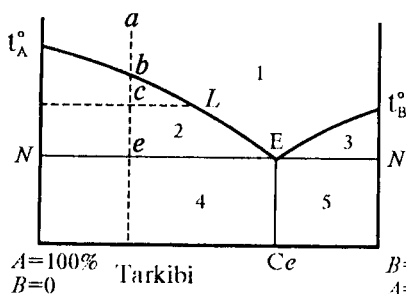
Moddalarning kondensatlangan (suyuq va qattiq) holatlarida bosimning ta'siri sezilarli bo'lmaganligidan «qattiq-suyuq» sistemalar muvozanatini o'rganishda bosimni o'zgarmas $P = \text{const}$ deb qabul qilinadi va shunga ko'ra Gibbsning fazalar qoidasi quyidagicha bo'ladi:

$$C + F = K + 1.$$

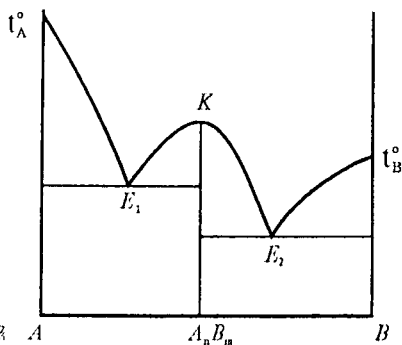
Agar $A - B$ moddalar suyuq holda cheksiz aralashib, o'zaro kimyoviy reaksiyaga kirishmasa va birikma hosil qilmasa, oddiy diagramma olinadi (VII.4-rasm).

t_A , t_B nuqtalar — A va B moddalarning suyuqlanish harorati. $t_A E$ chizig'i A modda suyuqlanish haroratining tarkib o'zgarishi bilan, ya'ni sistemaga qo'shilayotgan B moddaning miqdori o'zgarishi bilan o'zgarishini ko'rsatadi. C_e — evtektik tarkib, E — evtektik harorat. $t_A E t_B$ — suyuqlik egrisi (*likvidus*), $N - N$ chizig'i qattqlik egrisi (*solidus*) deyiladi. Suyuqlik chizig'idan yuqorida (1) faqat bir faza ko'rinishida bo'ladi.

$N - N$ — qattqlik egrisidan pastda (4, 5) sohalarida faqat qattiq faza bo'ladi. Bu oralikdagi (2, 3) sohalarida sistema geterogen bo'lib,

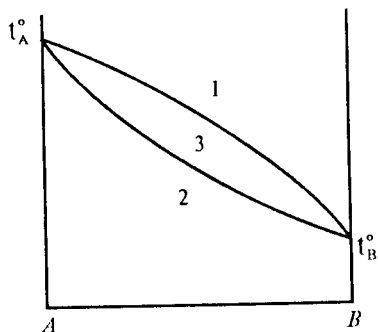


VII. 4-rasm. Oddiy diagramma.



VII. 5-rasm. Birikma hosil qiluvchi sistemaning holat diagrammasi.

qattiq (yoki cho'kma) va eritmadan iborat: 2-da A cho'kma + A — nisbatan to'yingan va B — nisbatan to'yinmagan eritma va xuddi shunday 3-da B ga nisbatan to'yingan, A ga nisbatan to'yinmagan eritma bo'ladi. E nuqtadagi sistemada A va B cho'kmalari hamda A va B nisbatan to'yingan eritma bo'ladi. Bu nuqtada $F = 3$, $C = 0$. Agar $N-N$ harorati biroz pasaytirilsa, evtektiv tarkib o'zgarmaydi va o'zgaras haroratda eritmada qolgan hamma A, B cho'kmaga tushadi. $N-N$ chizig'idan yuqorida turgan cho'kma —



VII. 6-rasm. Izomorf moddalarning holat diagrammasi:
1 — suyuqlanma;
2 — qattiq eritma;
3 — geterogen soha (kristall va eritma).

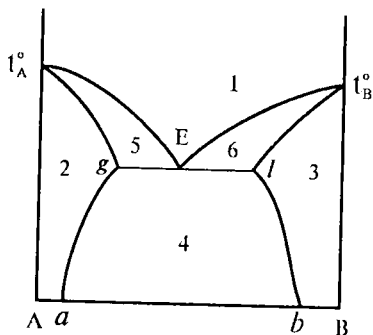
idiomorf va undan pastda turgan cho'kmalar — **evtektiv cho'kma** (kristall) deyiladi. 4-sohada A — **idiomorf** cho'kma va evtektiv aralashma (cho'kma) va 5-da B — **idiomorf** cho'kma va evtektiv aralashma (cho'kma holatida) bo'ladi.

a nuqtadagi eritma (suyuqlanma) sovitilsa, b nuqtada eritma A ga nisbatan to'yinadi va $b-e$ chizig'i bo'ylab A modda kristall holda cho'kmaga tushadi. C nuqtada qancha massa qattiq holda va qancha suyuqlanma holda borligini richag qoidasi orqali aniqlash mumkin, L nuqta suyuqlanma tarkibini ko'rsatadi.

Agar $A-B$ moddalar reaksiyaga kirishib birikma hosil qilsa, suyuqlik egrisi maksimumdan o'tadi va qancha xil birikma hosil bo'lsa, maksimum nuqtalar ham shuncha bo'ladi (VII. 5-rasm). Maksimum nuqtaga to'g'ri kelgan tarkib orqali abssissalar o'qidan birikmaning tarkibini aniqlash mumkin.

Qattiq holda bir-birida cheksiz eruvchi (qattiq eritma) hosil qiluvchi $A-B$ moddalarning holat diagrammasi VII. 6-rasmida berilgan.

Bir-biri bilan suyuqlanma holida cheksiz va qattiq holda cheklangan miqdorda eruvchi $A-B$ moddalarning holat diagrammasi VII. 7-rasmida berilgan.



VII. 7-rasm. Cheklangan konsentratsiyali qattiq eritma hosil qiluvchi sistemaning holat diagrammasi:

- a — nuqta B ning A dagi qattiq eritma hosil qilgandagi eruvchanligi; b — A ning B da eruvchanligi; 1 — suyuqlanma (gomogen); 4 — geterogen soha, A — B lar kristallarining aralashmasi; ab — B ning A dagi eruvchanligining harorat bilan o'zgarishi; bl — A ning B da eruvchanligining harorat bilan o'zgarishi; 2 — gomogen soha, B ning A dagi qattiq eritmasi; 3 — A ning B dagi qattiq eritmasi; 5 — A kristalli va suyuqlanma (eritma); 6 — B kristalli va suyuqlanma eritma.

MASALALAR

1. Rombik oltingugurt isitish natijasida $1,0133 \cdot 10^5 \text{ N/m}^2$ bosimda va $96,7^\circ\text{C}$ da monoklinik tuzilishdagi oltingugurtga $0,0000138 \text{ m}^3/\text{kg}$ hajm o'zgarishi bilan o'tadi. O'tish haroratining bosim bo'yicha o'zgarishi quyidagi koeffitsiyent orqali ifodalanadi:

$$\frac{dT}{dP} = 3,2567 \cdot 10^{-7} \text{ grad} \cdot \text{m}^2 / \text{N}.$$

Shu jarayonning o'tish issiqlik effektini toping.

2. Harorat $90,67 \text{ K}$ da metanning suyuqlanish issiqligini hisoblang. Bunda suyuqlanish haroratining $101,33 - 20266 \text{ kN/m}^2$ bosim oralig'idagi bog'lanishi quyidagicha ifodalanadi:

$$T_{\text{suyuq.}} = 90,667 + 2,6 \cdot 10^{-7} \cdot P - 6,147 \cdot 10^{-16} \cdot P^2.$$

Suyuqlanish vaqtidagi hajm o'zgarishi $2,69 \text{ sm}^3/\text{mol}$ ga teng.

3. Metanol $\Delta H_{\text{bug.}}$ harorat bilan quyidagi tenglamaga muvofiq o'zgaradi:

$$\frac{\Delta H_{\text{bug.}}}{T} = 1115,873 - 173,636 \ln T \text{ J/mol} \cdot \text{grad}.$$

Agar $64,7^\circ\text{C}$ da bosim 1 mm sim. ust. ga o'zgarsa, uning qaynash harorati qanchaga o'zgaradi?

4. Qalayning suyuqlanish issiqligi $59,413 \text{ J/g}$, suyuqlanish harorati 232°C , zichligi $7,18 \text{ g/sm}^3$, $dT/dP = 3,2567 \cdot 10^{-8} \text{ grad} \cdot \text{m}^2/\text{N}$ ga teng. 10 kg qalay suyuqlangandagi hajm o'zgarishini toping.

5. A va B moddalarning 323 K dagi bug' bosimlari mos ravishda $4,666 \cdot 10^4$ va $10,132 \cdot 10^4 \text{ N/m}^2$ (350 va 760 mm sim. ust.) ga teng. A moddadan $0,5 \text{ kmol}$, B moddadan $0,7 \text{ kmol}$ miqdorda aralashtirib, hosil qilingan eritma bilan muvozanatda bo'lgan bug'ning tarkibini hisoblang. Eritmani ideal eritma deb hisoblang.

6. Bir-birida aralashmaydigan dietilanilin va suvdan iborat sistema ustidagi bug' bosimi $372,4 \text{ K}$ da $10,132 \cdot 10^4 \text{ N/m}^2$ (760 mm sim. ust.) ga teng. Shu haroratda suv bug'i bosimi $9,919 \cdot 10^4 \text{ N/m}^2$ (744 mm sim. ust.). $0,1 \text{ kg}$ dietilanilinni haydash uchun qancha suv bug'i kerak bo'ladi?

7. Brombenzol suv bug'i bilan $368,3 \text{ K}$ da haydalganida bosim $10,132 \cdot 10^4 \text{ N/m}^2$ (760 mm sim. ust.) qiymatga ega. Brombenzol suvda umuman erimaydi. Shu haroratda suv va brombenzolning parsial bug' bosimlari mos ravishda $8,519 \cdot 10^4$ va $1,613 \cdot 10^4 \text{ N/m}^2$ (639 va 121 mm sim. ust.) ga teng. 1 kg suv bilan qancha miqdorda brombenzol haydalishini toping.

8. Suyuq simobning suyuqlanish issiqligi ($234,3 \text{ K}$ da) $11,8 \cdot 10^3 \text{ J/kg}$, zichligi 13690 kg/m^3 ($13,69 \text{ g/sm}^3$), qattiq simobning zichligi 14193 kg/m^3 ($14,193 \text{ g/sm}^3$). $235,33 \text{ K}$ da suyuqlanishdagi bosimni hisoblang.

9. Miqdori 1 kg bo'lgan TiCl_4 ni 298°C dan 423 K gacha qizdirishdagi issiqlik miqdorini toping. Issiqlik sig'implari $C_{r,q} = 156,9$; $C_{r,s} = 95,69$, suyuq holdagi TiCl_4 bug' bosimining harorat bo'yicha bog'lanishi quyidagiga teng:

$$\lg P = 8,56 - \frac{1450}{T}.$$

10. Bosim $1,0132 \cdot 10^5 \text{ N/m}^2$ (1 atm) bo'lganida xlorning bug'lanish issiqligini hisoblang. To'yingan bug' bosimining (N/m^2) suyuq xlor harorati bo'yicha bog'lanishi quyidagiga teng:

$$P = 3,58 \cdot 10^6 - 3,37 \cdot 10^4 + 30,11 \cdot T^2.$$

11. Freonning (CCl_2F_2) to'yingan bug' bosimining harorat bo'yicha o'zgarishi quyidagi tenglama bilan ifodalanadi:

$$\lg P = 34,5 - \frac{2406,1}{T} - 9,26 \cdot \lg T + 0,0037 T.$$

298 K da 1 mol freonning to'yingan bug' bosimi, ΔH_{bug} , ΔS , ΔG va ΔC_p ni aniqlang.

12. Harorat 272 K da suv bug'i va muz bosimlari farqini toping. Muzning suyuqlanish issiqligi $T = 273,16$ K da $3,34 \cdot 10^5$ J/kg (79,8 kal/g), $P_{\text{muz}} = P_{\text{suv}} = 6,104 \cdot 10^2$ N/m² (4,579 mm sim. ust.).

13. Naftalin $T = 353,3$ haroratda suyuqlanadi. Shu haroratda suyuqlanish issiqligi $147,639 \cdot 10^3$ J/kg ga teng. Solishtirma hajm farqi $\Delta V = V_s - V_q = 0,146 \cdot 10^{-3}$ m³/kg ga teng. Bosim $1,01 \cdot 10^3$ Pa ga o'zgarganda suyuqlanish harorati qanchaga o'zgaradi?

14. Sinil kislota bug' bosimining harorat bo'yicha o'zgarishi quyidagi tenglama bilan ifodalanadi:

$$\lg P = 9,16 - \frac{1237}{T},$$

T normal qaynash temperaturasi 299 K ga teng.

$P = 1,013 \cdot 10^5$ N/m² bo'lgandagi bug'lanish issiqligini toping.

15. Etil spirtining bug'lanish issiqligi $\Delta H = 887,644 \cdot 10^3$ J/kg. $T_1 = 343$ K haroratda to'yingan bug' bosimi $P_1 = 0,721 \cdot 10^5$ Pa ga teng. $T_2 = 353$ K da uning bug' bosimi qanchaga teng bo'ladi?

16. Qattiq va suyuq holdagi qalayning 505,1 K suyuqlanish haroratida zichliklari mos ravishda 6,988 va 7,184 g/sm³ ga teng. Qalay — $\Delta H_s = 7064,2$ J/mol. Bosim $1,01333 \cdot 10^7$ Pa da qalayning suyuqlanish haroratini aniqlang.

17. Metil spirtining 293,2 K haroratda bug' bosimi $125,3 \cdot 10^2$ Pa ga teng, 310,2 K haroratda esa $345,76 \cdot 10^2$ Pa ga teng. Shu

haroratlar chegarasida metil spirtning o'rtacha bug'lanish issiqligini toping.

18. Toluolning to'yingan bug' bosimi harorat bilan quyidagi tenglamaga muvofiq o'zgaradi:

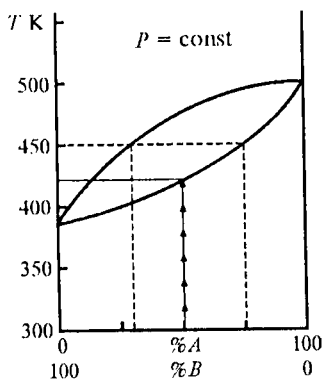
$$\lg P = -\frac{2866,53}{T} - 0,71 \lg T + 29,775.$$

Qaynash harorati $T = 383,30$ K dagi molar bug'lanish issiqligini aniqlang.

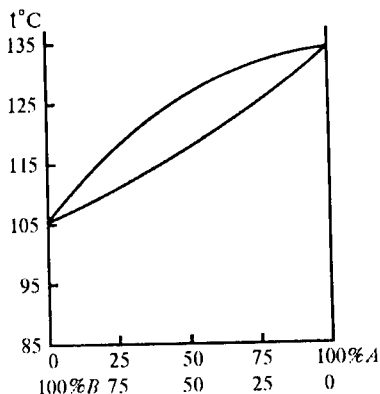
19. CCl_4 bug' bosimi harorat bilan quyidagicha o'zgaradi: $\lg P = 45812,8 - 44,01 \cdot T$. Suyuq CCl_4 $1,0133 \cdot 10^5$ Pa bosimda 348,2 K haroratda qaynaydi. CCl_4 ning 333,2 K dagi bug' bosimi qanchaga teng?

20. VII. 8-rasmda «tarkib — qaynash harorati» bo'yicha bir-birida cheksiz aralashadigan suyuqliklar holat diagrammasi keltirilgan. Harorat 450 K bo'lganida muvozanatdagi fazalar tarkibi va tarkibida 50% *A* modda tutgan suyuqlikning boshlang'ich qaynash haroratini toping.

21. VII. 9-rasmda keltirilgan diagrammadan foydalanib aralashma tarkibi 80 g *A* moddadan, 120 g *B* moddadan iborat bo'lganida



VII. 8-rasm.



VII. 9-rasm.

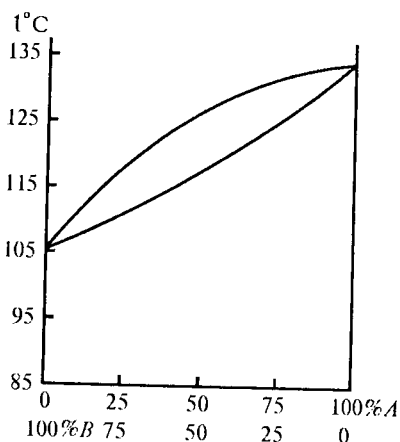
uning qaynash haroratini, shunday suyuqlik tarkibi bilan muvozanatda turgan bug' faza tarkibini toping.

22. Benzol va toluol aralashmalari ideal eritma bo'lib hisoblanadi. 80,1°C haroratda toza benzolning to'yingan bug' bosimi $1,013 \cdot 10^5$ Pa, toza toluolniki $0,4776 \cdot 10^5$ Pa ga teng. Tarkibida massasi bo'yicha 20% benzoli bor eritma bilan 80,1°C da muvozanatda turgan bug'ning tarkibini aniqlang.

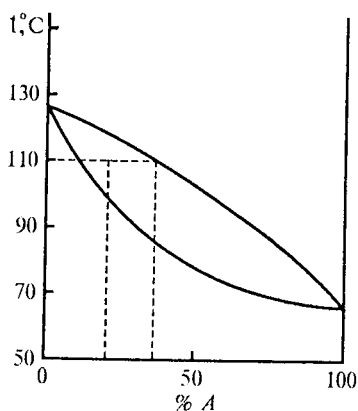
23. VII.10-rasmda binar eritma holat diagrammasi keltirilgan. Tarkibida 160 g *B* modda, 40 g *A* modda aralashishidan olingan eritmadan 110°C haroratda suyuq faza qolmasligi uchun aralashmaga *A* moddadan yana qancha qo'shish kerak bo'ladi?

24. VII.11-rasmda tarkibida 30 g *A*, 170 g *B* moddasi bor eritma holat diagrammasi berilgan. Shu eritmaning boshlang'ich qaynash harorati, bug' faza tarkibini aniqlang.

25. Tajriba asosida aseton va xloroformdan iborat ikki komponentli sistema uchun 308,2 K haroratda, tarkib bilan parsial bosim bo'yicha quyidagi natijalar olindi:



VII. 10-rasm.



VII. 11-rasm.

N_{CHCl_3}	0	0,2	0,4	0,6	0,8	1,0
$P_{\text{CHCl}_3} \cdot 10^{-4}, \text{N/m}^2$	0	4,453	1,09	1,98	3,00	3,91
$P_{(\text{CH}_3)_2\text{CO}} \cdot 10^{-4}, \text{N/m}^2$...	4,59	3,60	2,44	1,96	0,56	0

Shu qiymatlar asosida sistemaning holat diagrammasini chizing va $T = 308,26 \text{ K}$ haroratda tarkibida 50% CHCl_3 bor eritma qanday bosimda qaynay boshlashini aniqlang.

26. Tarkibida 0,5 kmol benzol va 0,5 kmol toluol bor eritma ustidagi bug' faza tarkibini toping. Ular uchun to'yingan bug' bosimlarining harorat bo'yicha bog'lanishi quyidagicha:

T, K	330	350	380	420
$P_{\text{C}_6\text{H}_6} \cdot 10^{-4}, \text{N/m}^2$	5,2	9,2	21,3	55,5
$P_{\text{C}_6\text{H}_5\text{CH}_3} \cdot 10^{-4}, \text{N/m}^2$	1,6	3,8	9,3	25,8

27. 0,1 kg naftalinni normal bosimda suv bug'i bilan haydash uchun qancha miqdorda suv bug'i kerak bo'ladi? Qaysi haroratda qaynash sodir bo'ladi? Amalda naftalin suvda erimaydi. Hisoblashlar uchun $P = f(T)$ bog'lanishning quyidagi natijalaridan foydalaning:

T, K	368	369	370	371	373
$P_{\text{H}_2\text{O}} \cdot 10^{-4}, \text{N/m}^2$	8,45	8,77	9,10	9,43	10,13
$P_{\text{C}_{10}\text{H}_8} \cdot 10^{-4}, \text{N/m}^2$	0,20	0,21	0,22	0,23	0,26

28. Aseton va uglerod (IV) sulfid (CS_2) uchun $T = 308,2 \text{ K}$ haroratda eritma ustidagi parsial bosim tarkib bo'yicha quyidagi qiymatlarga ega:

N_{CS_2}	0	0,2	0,4	0,6	0,8	1,0
$P_{\text{CS}_2} \cdot 10^{-4}, \text{N/m}^2$	0	3,73	5,04	5,67	6,13	6,83
$P_{(\text{CH}_3)_2} \cdot 10^{-4}, \text{N/m}^2$	4,59	3,87	3,40	3,07	2,53	0

Tarkib bo'yicha sistema parsial bosimining o'zgarish grafigini chizing (molar konsentratsiya ifodasi bo'yicha). $308,20 \text{ K}$ haroratda sistema bug' bosimi $8,5 \cdot 10^4 \text{ N/m}^2$ bo'lganida sistema qanday tarkibga ega bo'ladi?

29. Cu—Ni sistemasini sovitish natijasida olingan quyidagi qiymatlar asosida «tarkib — suyuqlanish harorati» holat diagrammasini chizing:

Ni, og'ir. %	0	20	40	60	80	100
T , kristallanishning boshlanishi, K	1373	1467	1554	1627	1683	1728
T , kristallanishning tugashi, K	1373	1406	1467	1543	1629	1728

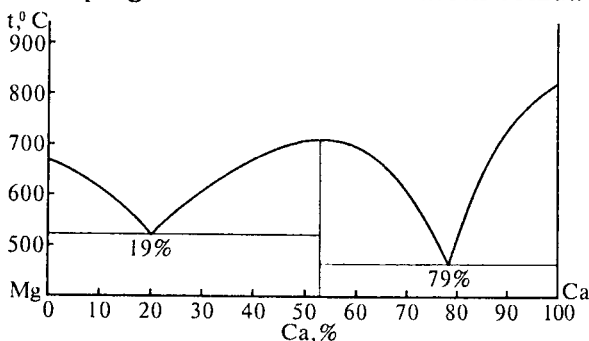
Tarkibida 30% Ni bor aralashma: 1) kristallanishning boshlanish haroratini; 2) qattiq eritmadan hosil bo'lgan birinchi kristallning tarkibini; 3) 0,24 kg shunday sistema 1470 K gacha sovitilganida suyuq va qattiq holdagi Ni miqdorini; 4) oxirgi suyuqlik tomchisining qotish haroratini; 5) suyuqlikning oxirgi tomchisi tarkibini aniqlang.

30. AgCl — KCl sistemasini sovitish natijasida quyidagi qiymatlar olingan:

AgCl, og'ir. %.....	0	20	40	60	80	100
T , kristallanishning boshlanishi, K	1055	958	837	688	631	728
T , kristallanishning tugashi, K	1055	984	584	584	584	728

Shu sistemaning «tarkib — suyuqlanish harorati» bo'yicha holat diagrammasini chizing. Suyuqlanish haroratini 650 K gacha pasaytirish uchun 1,7 kg AgCl ga qancha miqdorda KCl qo'shish kerakligini toping.

31. VII.12-rasmda Ca — Mg sistemasining suyuqlanish diagrammasi berilgan. Hosil bo'lgan kimyoviy birikmaning formulasini toping. Evtektika tarkibini atom-foizda ifoda qiling.



VII.12-rasm.

KO'P VARIANTLI MASALALAR

1. *A* moddadan iborat qattiq va suyuq holatdagi sistema to'yingan bug' bosimining haroratga bog'liq ravishda o'zgarish qiymatlari asosida quyidagilarni:

- a) T - R bog'lanish grafigini chizing va shunday nuqta toping;
- b) o'rtacha $\Delta H_{bug'}$ ni toping;
- d) dT/dP qiymatini suyuqlanish jarayoni uchun hisoblang;
- e) P (N/m^2) bosimda moddaning suyuqlanish haroratini aniqlang.

Variantlar	Qattiq holatda		Suyuq holatda		Sharoiti
	T, K	$P, N/m^2$	T, K	$P, N/m^2$	
1	2	3	4	5	6
1	268,2	401,2	269,2	505	$M=18$ $P=40,5 \cdot 10^5$ $d_{qat.}=918$ $d_{suyuq}=1000$
	269,2	437,2	271,2	533	
	270,2	475,9	273,9	573	
	271,2	517,2	275,2	656	
	272,2	553,2	278,2	760	
			299,2	1600	
2	248	7998	260	23300	$M=27$ $P=800 \cdot 10^5$ $d_{qat.}=718$ $d_{suyuq}=709$
	254,4	13300	265	27190	
	258	17995	270	31860	
	259	19995	278	40290	
	260	23327	280	40555	
			282	47990	

1	2	3	4	5	6
3	196	101325	212	592751	$M=44$
	203	190491	220	648480	$P=750 \cdot 10^5$
	213	402360	223	674824	$d_{qat} = 1542$
	220	648480	241	1065237	$d_{suyuuq} = 1510$
			242	1131722	
4	230	26260	236	63315	$M=52$
	233	31458	246	78647	$P=350 \cdot 10^5$
	237	39990	248	83979	$d_{qat} = 3010$
	240	49987	249	86645	$d_{suyuuq} = 2955$
	243	58518	251	96942	
	245	66650	252	100508	
5	183,2	333,3	201	4665,5	$M=64$
	188,0	586,5	204	5305	$P=1000 \cdot 10^5$
	196,0	1850	214	7198	$d_{qat} = 1600$
	199,2	3000	219	7998	$d_{suyuuq} = 1560$
	203,7	5305	230,2	13328	
			233	21728	
6	177,3	15996	180	26600	$M=81$
	180	19995	185,5	32992	$P=300 \cdot 10^5$
	182	23994	188	37057	$d_{qat} = 1625$
	184	28659	191	43456	$d_{suyuuq} = 1610$
	185,5	31992	194	51987	
			197	59985	
7	353,2	39,99	363,2	186,6	$M=122$
	363,2	79,99	393,2	679,8	$P=850 \cdot 10^5$
	373,2	186,6	395,2	733,1	$d_{qat} = 1105$
	383,2	393,2	400,7	973,1	$d_{suyuuq} = 1095$
	393,2	679,8	403,7	1133	
			408,7	1399,6	
8	223,2	133,3	244,2	1299	$M=154$
	237,2	466,5	253,2	1319	$P=6,08 \cdot 10^5$
	246,2	799,8	270,1	2465	$d_{qat} = 1680$
	252,2	1213	286,5	3865	$d_{suyuuq} = 1650$
	253,2	1319	292,2	4398	
			303,2	7664	

2. Turg'un bosimda A va B moddalar uchun turli haroratda muvozanatda turgan suyuqlik va bug' fazalarning tarkibi A modda orqali berilgan. A moddaning suyuq fazaning mol foiz ifodasidagi tarkibi x va bug' fazaning tarkibi y ga teng. Tarkib foiz orqali berilgan, keltirilgan ma'lumotlardan foydalanib quyidagilarni bajaring:

1) turg'un bosimda suyuq va bug' fazalarning tarkib diagrammasi (holat diagrammasi)ni chizing;

2) a % A mol bo'lgan aralashmaning qaynash haroratini aniqlang;

3) T_1 haroratda qaynaydigan aralashmaning suyuq va bug' fazasi tarkibini aniqlang;

4) b kg A va c kg B moddalardan iborat aralashma haydalganda qaysi modda va qancha miqdorda ajralib chiqadi?

5) a % A modda tutgan 2 kg aralashma T_1 haroratgacha qaynatilganda A moddaning qanchasi suyuqlik va qanchasi bug' fazada bo'ladi?

Variantlar	Sistema	$P \cdot 10^{-4}$, Pa	A moddaning tarkibi, mol %		T, K
			x—suyuq fazada	y—bug' fazada	
1	2	3	4	5	6
1	A—HNO ₃ B—H ₂ O	10,133	0,0	0,0	373
			8,4	0,6	380
			12,3	1,8	385
			22,1	6,6	391,6
			30,8	16,6	394,6
			38,3	38,3	394,9
			40,2	60,2	394,0
			53,0	89,1	385,0
			61,6	92,5	372,0
			100,5	100,0	357
2	A—HNO ₃ B—CH ₃ COOH	10,79	0,0	0,0	391,1
			10,0	3,0	395,0
			20,0	8,0	400,0
			33,3	34,0,	401,6
			40,0	47,0	400,3
			50,0	82,0	393,3
			60,0	96,0	378,0
			100,0	100,0	358,3

1	2	3	4	5	6
3	A—H ₂ O	10,133	0,0	0,0	435,0
			4,0	19,0	427,8
			6,0	36,0	419,0
			10,0	81,1	382,5
			20,0	89,0	373,6
			30,0	90,5	371,7
			90,0	90,8	370,9
			96,0	90,9	370,9
			100,0	100,0	373,0
4	A—CS ₂ B—CH ₃ COCH ₃	10,138	0,0	0,0	329,2
			1,9	8,3	327,0
			4,8	18,5	324,4
			13,4	35,1	319,6
			18,6	44,3	317,0
			38,0	57,4	313,3
			53,6	62,7	312,3
			78,9	70,5	312,3
			96,8	88,6	316,5
			100,0	100,0	319,3
5	A—CH ₃ OH	9,670	0,0	0,0	351,6
			2,4	17,5	341,2
			4,7	43,5	333,3
			6,3	53,4	330,3
			9,2	54,6	329,8
			24,9	59,9	329,4
			78,5	66,6	329,9
			84,7	71,3	330,6
			94,1	84,4	332,6
			100,1	100,0	336,1

1	2	3	4	5	6
6	$A-CH_3COCH_3$	10,0	0,0	0,0	352,8
			4,0	15,1	348,2
			15,9	35,3	342,5
			29,8	40,5	341,5
			42,1	43,6	340,8
			53,7	46,6	641,0
			71,8	54,9	342,0
			87,2	68,3	344,8
			93,9	78,7	347,4
7	$A-CH_3COCH_3$ $B-CH_3OH$	10,133	0,0	0,0	337,7
			4,8	14,0	335,9
			17,6	31,7	333,1
			28,0	42,0	331,3
			40,0	51,6	330,2
			60,0	65,6	329,1
			80,0	80,0	328,6
			90,0	94,0	328,8
			99,0	97,0	329,1
			100,0	100,0	329,5
8	$A-C_2H_5-O-C_2H_5$ $B-C_6H_{12}O_2$	2,200	0,0	0,0	353,6
			16,1	21,0	351,2
			31,3	37,5	349,9
			47,6	47,6	349,4
			61,3	57,8	349,5
			77,7	70,5	350,2
			87,3	80,7	351,3
			100,0	100,0	353,3

Variant-lar	1	2	3	4	5	6	7	8
T_1	388	393	372	317	331	345	329,5	350,5
a	55	60	50	25	80	75	60	75
b	81	61,2	15,8	30,4	62,2	64	73	65,5
c	19	38,8	84,2	69,6	37,8	36	27	34,5

3. Yuqorida 2-jadvalda keltirilgan umumiy bosim va suyuqlik ustidagi bug' tarkibidan foydalanib, suyuq fazadagi A komponentning aktivligi va aktivlik koeffitsiyentini toping.

Variant-lar	Sistema	$P \cdot 10^{-4} \text{Pa}$	A moddaning mol, % miqdori	T, K
1	$\text{HNO}_3\text{—H}_2\text{O}$	10,133	53,0	385,0
2	$\text{HNO}_3\text{—C}_2\text{H}_4\text{O}_2$	10,079	60,0	378,0
3	$\text{H}_2\text{O—C}_6\text{H}_4\text{O}_2$	10,133	8,0	395,5
4	$\text{CS}_2\text{—C}_3\text{H}_6\text{O}$	10,133	13,4	319,6
5	$\text{CH}_3\text{OH—C}_6\text{H}_6$	9,670	5,9	330,7
6	$\text{C}_2\text{H}_6\text{O—C}_6\text{H}_6$	10,000	4,0	348,2
7	$\text{C}_6\text{H}_6\text{O—CH}_3\text{OH}$	10,133	17,6	333,1
8	$\text{C}_4\text{H}_{10}\text{O—C}_6\text{H}_{12}\text{O}_2$	2,200	16,1	351,2

VIII bob

ELEKTROLIT ERITMALAR. ERITMALARNING ELEKTR O'TKAZUVCHANLIGI

Noelektrolit eritmalar faqat neytral molekulalardan iborat bo'lsa, elektrolit eritmalar (kislota, asos, tuz eritmaları) elektrolitik dissotsilanish natijasida neytral molekulalar bilan birga zaryadlangan moddalar — ionlar mavjud va dissotsilanish sababli zarrachalarning soni ko'payadi. Shunga ko'ra, bir xil konsentratsiyada elektrolit eritmalarining tajribada topilgan osmotik bosimi, bug' bosimi, qaynash haroratining ortishi, muzlash haroratining pasayishi va hokazolar noelektrolit eritmanikiga qaraganda katta bo'ladi. Noelektrolit eritmalar qonuni elektrolit eritmalariga to'g'ri kelishi uchun ularga i — koeffitsiyentini ko'paytirish kerak: $i > 1$ bo'ladi. i — *izotonik* yoki *Vant-Goff koeffitsiyenti* deyiladi, u zarrachalar soni qanchalik ortishini ko'rsatadi.

noelektrolit eritmalar
(nazariy)

elektrolit eritmalar
(tajribada)

$$\text{Osmotik bosim } (P_{osm})_{naz} = cRT. \quad (P_{osm})_t = (ic)RT \quad (\text{VIII.1})$$

$$\text{Muzlash haroratining pasayishi } (\Delta T_t)_{naz} = kC; \quad (\Delta T_m)_t = ikC \quad (\text{VIII.2})$$

$$\text{Qaynash haroratining ortishi } (\Delta T_q)_{naz} = EC; \quad (\Delta T_q)_{naz} = iEC \quad (\text{VIII.3})$$

$$\text{Bug' bosimi } \frac{P^0 - P}{P^0} = \frac{\Delta p}{P^0} = \frac{n_2}{n_1 + n_2}; \quad \frac{P^0 - P}{P^0} = \frac{\Delta p}{P^0} = \frac{in_2}{n_1 + n_2}; \quad (\text{VIII.4})$$

$$\text{Molekular massa } (M)_{naz} = \frac{E \cdot g \cdot 1000}{G \cdot \Delta T}; \quad (M)_m = \frac{iE \cdot g \cdot 1000}{G \cdot \Delta T}. \quad (\text{VIII.5})$$

Bu tenglamalardan:

$$i = \left(\frac{\Delta P_t}{\Delta P_n} \right)_{osm.b.} = \left(\frac{\Delta T_t}{\Delta T_n} \right)_m = \left(\frac{\Delta T_q}{\Delta T_n} \right)_q = \frac{\Delta P_t}{\Delta P_n}. \quad (\text{VIII.6})$$

t , n — amalda (tajribada) va nazariy (noelektrolit eritmalar tenglamalariga muvofiq) hisoblab topilgan kattaliklar qiymati.

Elektrolitlarning dissotsilanish qobiliyatini **dissotsilanish darajasi** (η) ifodalaydi:

$$\alpha = \frac{C}{C_0} = \frac{\text{dissotsilangan molekularlar (mollar) soni}}{\text{molekulalarning dastlabki umumiy soni (mollar)}} \quad (\text{VIII.7})$$

va ionlar konsentratsiyasi $C = \alpha \cdot C_0$. (VIII.8)

α ning qiymatiga qarab hamma elektrolitlar ikki sinfga bo'linadi. **Kuchsiz elektrolitlar** $\alpha < 1$ bo'lib (faqat cheksiz suyultirilganda $\alpha = 1$), eritma suyultirilgan sari α oshadi. **Kuchli elektrolitlar** hamma konsentratsiyada to'la dissotsilangan, ya'ni doimo $\alpha = 1$ bo'ladi. Bu ikki sinf elektrolitlari xossalari bilan farq qiladi.

VIII.1. KUCHSIZ ELEKTROLITLAR

Dissotsilanish darajasi α bilan i quyidagicha bog'langan:

$$\alpha = \frac{i-1}{n-1}. \quad (\text{VIII.9})$$

n molekularlar dissotsilanganda hosil bo'lgan ion xillarining soni NH_4OH , CH_3COOH — 2 ga, NaCl — 2, CuCl_2 — 3, AlCl_3 — 4 ga teng va hokazo.

Dissotsilanish muvozanati. Dissotsilanish jarayoni qaytar jarayondir. Masalan, binar AB elektrolit uchun:

$$AB \rightleftharpoons A^+ + B^-$$

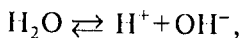
$$K_D = \frac{[A^+][B^-]}{[AB]} = \frac{C_0\alpha \cdot C_0\alpha}{C_0 - C_0\alpha} = \frac{\alpha^2}{1-\alpha} C_0, \quad (\text{VIII.10})$$

K_D — dissotsilanish muvozanat konstantasi;

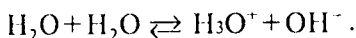
C_0 — elektrolit eritma konsentratsiyasi.

$[AB]$ dissotsilanmagan molekular konsentratsiyasi.

Suvning dissotsilanishi. Suv juda kam miqdorda bo'lsa ham dissotsilanadi:



aniqrog'i eritmada vodorod ioni emas, gidroksoniy (H_3O^+) ioni bo'ladi, ya'ni:



Muvozanat konstantasi tenglamasini dissotsilanish jarayoni uchun yozsak,

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}.$$

suv juda kam dissotsilanganidan $[\text{H}_2\text{O}]$ ni o'zgarmas (const) deb qabul qilish mumkin:

$$\begin{aligned} K_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}] &= [\text{H}^+][\text{OH}^-] = \text{const} \\ K_b &= [\text{H}^+][\text{OH}^-]. \end{aligned} \quad (\text{VIII.11})$$

K_b — *suvning ion ko'paytmasi* deyiladi.

K_b turg'un bo'lganligidan eritmaning muhit reaksiyasini (kislotali, asosli) H^+ va OH^- larda birining konsentratsiyalari orqali ifoda qilish mumkin. Vodorod ion H^+ — konsentratsiyasi orqali ifoda qilish qabul qilingan:

$$\text{pH} = -\lg[\text{H}^+] \text{ va } [\text{H}^+] = 10^{-\text{pH}}; \quad [\text{OH}^-] = \frac{K_b}{[\text{H}^+]}. \quad (\text{VIII.12})$$

Kislotali muhitda $\text{pH} < 7$, asosli muhitda $\text{pH} > 7$ bo'ladi.

Real eritmalar va elektrolit eritmalar uchun:

$$\text{pH} = -\lg a_{\text{H}^+}; \quad a_{\text{H}^+} = 10^{-\text{pH}}, \quad (\text{VIII.13})$$

bunda: a — termodinamik aktivlik.

Bufer eritmalar. Bufer eritmalar ma'lum haroratda muayyan pH ga ega bo'ladi. Ularga kuchli kislota yoki kuchli ishqordan ozgina qo'shilsa, ularning pH i deyarli o'zgarmaydi yoki juda kam o'zgaradi. Bufer eritmalar asosan ikki xil bo'ladi:

a) kuchsiz kislota va shu kislotalaning kuchli ishqor bilan bergan tuzi aralashmasi (masalan: $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$);

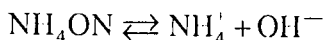
b) kuchsiz asos va shu asosning kuchli kislota bilan hosil qilgan tuzi aralashmasi, (masalan: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$).

Birinchi tipdagi bufer eritmaning $[\text{H}^+]$ va pH larini quyidagicha hisoblash mumkin:

$$[H^+] = K_k \cdot \frac{[kislota]}{[tuz]}; \text{ pH} = -\lg K_k + \lg \frac{[tuz]}{[kislota]}. \quad (\text{VIII.14})$$

Agar kislota ning ma'lum haroratda dissotsilanish darajasi (α) e'tiborga olinsa: $[H^+] = K_k \frac{[kislota]}{\alpha[tuz]}$.

Ikkinchi xildagi bufer critmaning (H^+) va pH:



$$K_a = \frac{[NH_4^+][OH^-]}{[NH_4OH]}; \text{ bundan } [OH^-] = \frac{K_a[NH_4OH]}{[NH_4^+]} = \frac{K_a[asos]}{[tuz]}$$

$$[H^+] = \frac{K_b}{[OH^-]} = \frac{K_b[tuz]}{K_a[asos]}$$

$$\text{pH} = -\lg \frac{K_b}{K_a} + \lg \frac{[asos]}{[tuz]} \quad \text{ga teng bo'ladi.} \quad (\text{VIII. 15})$$

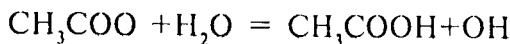
K_k, K_a — kislota va asosning dissotsilanish muvozanat konstantalari;
 K_b — suvning ion ko'paytmasi.

Tuzlarning gidrolizi. Tuz ionlarining suv ionlari bilan reaksiyaga kirishishi **gidroliz** deyiladi: natijada tuzning tabiatiga qarab muhit kislotali yoki asosli tabiatga ega bo'ladi.

Kuchsiz kislota va kuchli asosdan hosil bo'lgan tuz, masalan, CH_3COONa quyidagicha gidrolizlanadi va muhit asosli bo'ladi:



yoki



Gidroliz konstantasi K_r :

$$K_r = \frac{C_{CH_3COOH} \cdot C_{OH^-}}{C_{CH_3COO^-}} = \frac{\beta_2}{1-\beta} C_O = \frac{K_b}{K_k}. \quad (\text{VIII.16})$$

β — gidrolizlanish darajasi bo‘lib:

$$\beta = \frac{C}{C_0} \frac{(\text{gidrolizlangan molekular soni})}{(\text{molekulalarning (mollar) umumiy soni})}$$

$\beta < 1$ bo‘lganligidan $(1 - \beta) = 1$ qabul qilinsa:

$$K_r = C_0 \beta^2 = \frac{C_0^2 \beta^2}{C_0} = \frac{C_{\text{OH}^-}^2}{C_0}$$

va

$$C_{\text{OH}^-} = \sqrt{K_r \cdot C_0}; \quad \beta = \sqrt{\frac{K_r}{C_0}} = \sqrt{\frac{K_b}{K_k \cdot C_0}};$$

$$C_{\text{H}^+} = \frac{K_b}{C_{\text{OH}^-}} = \sqrt{\frac{K_b K_k}{C_0}} \quad (\text{VIII. 17})$$

va

$$\text{pH} = -\lg C_{\text{H}^+} = -\frac{1}{2} \lg K_b - \frac{1}{2} \lg K_k + \frac{1}{2} \lg C_0; \quad (\text{VIII. 18})$$

bunda: K_k — kislota ning dissotsilanish konstantasi; K_b — suvning ion ko‘paytmasi; C_0 — critma konsentratsiyasi.

Kuchli kislota va kuchsiz asosdan hosil bo‘lgan tuz (NH_4Cl) uchun:

$$\text{pH} = -\frac{1}{2} \lg K_b + \frac{1}{2} \lg K_a - \frac{1}{2} \lg C_0, \quad (\text{VIII.19})$$

bunda: K_a — asosning dissotsilanish konstantasi.

Eruvchanlik ko‘paytmasi. Bu tushuncha qiyin eruvchi tuzlar uchun (masalan, AgCl) xos bo‘lib, eruvchanlik ko‘paytmasi (L)

to'yingan eritmada ionlar konsentratsiyasining ko'paytmasiga teng. Masalan, AgCl uchun:

$$L_{\text{AgCl}} = [\text{Ag}^+] [\text{Cl}^-]. \quad (\text{VIII.20})$$

Eruvchanlik ko'paytmasi ma'lum elektrolit uchun ma'lum haroratda o'zgarmas qiymatga ega. Tuz erituvchida ionlar konsentratsiyasi ko'paytmasi eruvchanlik ko'paytmasiga yetguncha eriydi, undan ortganidan so'ng cho'kma tusha boshlaydi. Har qaysi ionning eritmadagi konsentratsiyasi **eruvchanlik** (C) deyiladi va demak:

$$C = \sqrt{L}.$$

VIII.2. ELEKTROLITLARNING ELEKTR O'TKAZUVCHANLIGI

Elektrolitlarda elektr zaryadi (oqimi)ni ionlar tashib o'tadi. Elektr o'tkazuvchanlik qarshilikka teskari kattalikdir. Kuzatilgan qarshilik R :

$$R = \rho \frac{l}{S},$$

bunda: l — o'tkazgichning uzunligi; ρ — solishtirma qarshilik.

$$\frac{1}{R} = \lambda_k; \quad \frac{1}{\rho} = \lambda_s. \quad (\text{VIII.21})$$

$$\lambda_k = \lambda_s \cdot \frac{S}{l}, \quad (\text{VIII.22})$$

λ_k — kuzatilgan elektr o'tkazuvchanlik,

λ_s — *solishtirma elektr o'tkazuvchanlik*, bir-biridan 1 m (1 sm) oraliqda joylashgan va yuzasi 1 m² (1 sm²) bo'lgan tekis elektrodlar oralig'ida joylashgan eritma hajmining elektr o'tkazuvchanligi. O'lchami $\Omega^{-1} \cdot \text{sm}$.

Kuzatilgan elektr o'tkazuvchanlik ko'pincha *ekvivalent elektr o'tkazuvchanlik* λ_e bilan ifodalanadi. Bu bir-biridan 1 m (1 sm) oraliqda joylashgan va 1 kg-ekvivalent (1 gramm-ekvivalent) erigan moddada tutgan eritma hajmining elektr o'tkazuvchanligidir. Bu ikki ifoda quyidagicha bog'langan:

$$\lambda_e = \lambda_s V \quad \text{yoki} \quad \lambda_e = \frac{\lambda_s}{C}. \quad (\text{VIII.23})$$

Avvallari qo'llanilgan o'lchov birliklari bo'yicha:

$$\lambda_e = \frac{\lambda_s \cdot 1000}{C}; \quad \lambda_e = 1000 \lambda_s V. \quad (\text{VIII.24})$$

V — suyultirish bo'lib, 1 kg-ekv (g-ekv) erigan modda tutgan eritma hajmiga teng.

C — eritmaning g-ekvivalenti (g-ekv) bilan ifodalangan konsentratsiyasi bo'lib, uning o'lchami $\Omega^{-1} \cdot \text{m}^2$ (kg-ekv), $\Omega^{-1} \cdot \text{sm}^2$ (g-ekv).

Ba'zan *molar elektr o'tkazuvchanlik* λ_m bilan ham ifodalanadi.

Kuchsiz elektrolitlarda eritma suyultirilgani sari λ_e ortib boradi va cheksiz suyultirilganda o'zining maksimal qiymatiga yetadi hamda bunda elektr o'tkazuvchanlik cheksiz suyultirilgandagi ekvivalent o'tkazuvchanlik deyiladi (λ_∞). Kolraush qonuniga muvofiq:

$$\lambda_\infty = \lambda_+ + \lambda_-. \quad (\text{VIII.25})$$

U_0 , V_0 — cheksiz suyultirilgan eritmada kation va anionning mutlaq tezligi — 298,2 va elektr maydon kuchlanishi 1 voltga teng bo'lgandagi tezligi. Ma'lum elektr maydoni kuchlanishida tezlik:

$$U = U_0 E, \quad V = V_0 E, \quad (\text{VIII.26})$$

$$\alpha = \frac{\lambda_e}{\lambda_\infty}, \quad (\text{VIII.27})$$

bunda: λ_e — ma'lum konsentratsiyadagi ekvivalent elektr o'tkazuvchanlik.

$$K_D = \frac{\alpha^2 C_0}{1 - \alpha} = \frac{\lambda_e^2 C_0}{\lambda_\infty (\lambda_\infty - \lambda_e)}. \quad (\text{VIII.28})$$

Bu Ostvaldning suyultirish qonuni bo'lib, $\lambda_e = \varphi(c)$ bog'liqlikning analitik ifodasidir.

n_+ , n_- — kation va anionning tashish soni bo'lib, shu ionning umumiy elektr miqdorining qancha qismini tashib o'tganini ko'rsatadi, ya'ni:

$$n_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{U_0}{U_0 + V_0} = \frac{\lambda_+}{\lambda_\infty}; \quad n_- = \frac{\lambda_-}{\lambda_+ + \lambda_-} = \frac{V_0}{V_0 + U_0} = \frac{\lambda_-}{\lambda_\infty} \quad (\text{VIII.29})$$

va

$$n_+ + n_- = 1; \quad \frac{n_+}{n_-} = \frac{U_0}{V_0}; \quad (\text{VIII.30})$$

$$\lambda_+ = n_+ \cdot \lambda_\infty; \quad (\text{VIII.31})$$

$$\lambda_- = n_- \cdot \lambda_\infty. \quad (\text{VIII.32})$$

Tashish sonlari qiymati elektr oqimi o'tgandagi elektrod atrofida eritma konsentratsiyasi o'zgarishini o'lchash bilan aniqlanadi:

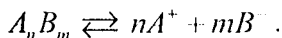
$$n_+ = \frac{P_a}{P_a + P_k}; \quad n_- = \frac{P_k}{P_a + P_k}, \quad (\text{VIII.33})$$

bunda: P_a , P_k — anod va katod maydonlarida eritma konsentratsiyasining o'zgarishi.

VIII.3. KUCHLI ELEKTROLITLAR

Termodinamik aktivlik. Elektrolit eritmalar konsentratsiyasi o'zgarishi bilan ularning xossalari (bug' bosimi, elektr o'tkazuvchanlik va hokazolar) ham o'zgaradi va bu bog'lanishlar ma'lum tenglamalar orqali ifodalanadi. Kuchsiz elektrolitlarda bunga asosiy sabab eritma konsentratsiyasi o'zgarishi bilan dissotsilanish darajasining o'zgarishi, ya'ni ionlarning eritmada nisbiy miqdorining o'zgarishidir. Kuchli elektrolitlar hamma konsentratsiyada to'la dissotsilangan bo'ladi, ya'ni konsentratsiya o'zgarishi bilan ionlar nisbati o'zgarmaydi. Kuchli elektrolitlarda konsentratsiya o'zgarishi bilan uning xossalari ham o'zgarishiga sabab molekullarning umumiy soni o'zgarishi bilan bir qatorda ionlar o'zaro ta'sirining o'zgarishidir. Shunga ko'ra, konsentratsiyaning o'zgarishi kuchli elektrolitlarning xossalari mutanosib (proporsional) holda namoyon bo'lmaydi. Konsentratsiya bilan bir qatorda ionlarning o'zaro ta'sirini e'tiborga olgan va xossada to'g'ridan-to'g'ri namoyon bo'ladigan «konsentratsiya» ifodasiga **termodinamik aktivlik** deyiladi. Kuchli elektrolitlarga mansub tenglamalardagi aniq hisoblarda konsentratsiya ifodasi o'rniga termodinamik aktivlik qo'yish kerak. Termodinamik aktivlik (a)ning ikki xil ifodasi mavjud: o'rtacha molekular a va o'rtacha ion aktivlik (a).

Agar eritma quyidagicha dissotsilansa,



O'rtacha molal aktivlik:

$$a = a_+^n a_-^m \text{ ga teng.} \quad (\text{VIII.34})$$

O‘rtacha ion aktivligi:

$$a_{\pm} = (a_+^n \cdot a_-^m)^{\frac{1}{N}}; \quad N = n + m, \quad (\text{VIII.35})$$

a_+ , a_- — kation va anionning termodinamik aktivligi. Demak, bu ikki xil aktivlik ifodasi quyidagicha bog‘langan:

$$a = a_{\pm}^N \quad (\text{VIII.36})$$

$$a_{\pm} = \gamma_{\pm} C_{\pm}. \quad (\text{VIII.37})$$

$\gamma_{\pm}$ — ionlarning o‘rtacha termodinamik aktivlik koeffitsiyenti bo‘lib, ionlarning o‘zaro ta‘sirini e‘tiborga oladi. $C_{\pm}$ — ionlarning o‘rtacha molal konsentratsiyasi bo‘lib,

$$\gamma_{\pm} = (\gamma_+^n \cdot \gamma_-^m)^{\frac{1}{N}}; \quad C_{\pm} = (C_+^n \cdot C_-^m)^{\frac{1}{N}}. \quad (\text{VIII.38})$$

VIII.4. ELEKTROLIT ERITMALARNING ION KUCHI

Agar $\gamma_{\pm}$ ma’lum bo‘lsa, xohlagan konsentratsiyada a ning qiymatini hisoblash mumkin. Shunga ko‘ra, odatda $\gamma_{\pm}$ o‘lchanadi yoki aniqlanadi. Eritmada ma’lum ionning o‘rtacha ion aktivlik koeffitsiyenti eritma tabiatiga, ya’ni qanday elektrolit moddalarning majmuidan iboratligiga boq‘liq bo‘lmasdan, eritmaning **ion kuchi** deb atalgan kattalikka boq‘liq bo‘ladi.

Eritmaning ion kuchi ionlarning zaryadi va konsentratsiyasiga boq‘liq bo‘lgan kattalik bo‘lib, u ionlar molalligini (molarligini) ularning zaryadlari kvadratiga ko‘paytmasi yarmiga teng, ya’ni:

$$J = \frac{1}{2} \sum C_i \cdot Z_i^2. \quad (\text{VIII.39})$$

Ion kuchini bilgan holda kuchli elektrolitlarning oʻrtacha aktivlik koeffitsiyentini aniqlash mumkin. Oʻta suyultirilgan eritmalar uchun Debay-Gyukkel tenglamasi:

$$\lg \gamma_{\pm} = -A\sqrt{J}. \quad (\text{VIII.40})$$

A — turgʻun kattalik boʻlib, suv uchun $A = 0,509$ ga teng. Oʻta kuchli suyultirilgan eritma uchun J ni konsentratsiya (C) bilan almashtirish mumkin:

$$\lg \gamma_{\pm} = -A\sqrt{C}. \quad (\text{VIII.41})$$

Biroz konsentrlangan eritma uchun:

$$\lg \gamma_{\pm} = \frac{Z_+ Z_- A\sqrt{J}}{1 + J}. \quad (\text{VIII.42})$$

Kuchli elektrolitlarning elektr oʻtkazuvchanligi uchun Kolraush qonuni boʻyicha:

$$\lambda_e = \lambda_{\infty} - a\sqrt{c}, \quad (\text{VIII.43})$$

a — har qaysi elektrolit uchun erituvchi va haroratga bogʻliq turgʻun kattalik.

Yuqorida bayon etilganidek, kuchli elektrolitlarga mansub aniq hisoblarda termodinamik aktivlik eʼtiborga olinishi kerak. Konsentratsiya ifodasi oʻrniga termodinamik aktivlikni qoʻyish kerak. Masalan, AgCl uchun quyidagini

$$L = C_{\text{Ag}^+} \cdot C_{\text{Cl}^-} \quad L = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} \quad (\text{VIII.44})$$

qoʻllash kerak.

MASALALAR YECHISHGA DOIR MISOLLAR

1. 2 l da 143 g MgCl_2 erigan eritma — $3,7^\circ\text{C}$ da muzlaydi. Suvning krioskopik konstantasi $E = 1,86$ ga teng. Dissotsilanish darajasi (α) ni aniqlang.

Yechish. Tarkibdan eritmaning molal konsentratsiyasi (m) ni aniqlash mumkin. Eritma konsentratsiyasi va muzlash harorati berilgan. Bu ma'lumotlardan foydalanib bevosita α ni aniqlash mumkin emas. Chunki $\alpha = f(s_g, t_m)$ bog'langan bevosita tenglama yo'q.

α — qanday kattalik bilan bevosita bog'langanligini va bu kattalikni masala shartidan keltirib aniqlash mumkinligini topamiz. α bevosita (VIII.9) tenglama bo'yicha i bilan bog'langan. Demak, i ma'lum bo'lsa, α ni aniqlash mumkin.

i ni esa (VIII.6) tenglamadan hisoblab topish mumkin.

Buning uchun nazariy muzlash haroratini bilish kerak.

Nazariy muzlash haroratini (VIII.2) tenglamadan foydalanib aniqlaymiz.

$$\begin{array}{c} \text{Shunday qilib, tartib} \\ \xrightarrow{\text{teng. (VIII.6)}} i \xrightarrow{\text{teng. (VIII.9)}} \alpha \end{array} \quad \begin{array}{c} \xrightarrow{\text{teng. (VIII.2)}} m \xrightarrow{\text{teng. (VIII.2)}} t_{\text{muz(nazariy)}} \end{array}$$

Shu tartibda masala yechiladi: $M_{\text{MgCl}_2} = 24,2 + 35,52 = 95,3$

$$\left. \begin{array}{l} \left(\frac{143}{95,3} \right) \frac{2000}{1000} \\ m \frac{2000}{1000} \end{array} \right\} m = \frac{143 \cdot 1000}{95,3 \cdot 2000} = 0,75$$

$$\Delta t_{m(naz)} = E_m = \frac{1,86143 \cdot 1000}{95,3 \cdot 2000} = 1,39,$$

$$i = \frac{\Delta t_{raj}}{\Delta t_{naz.}} = \frac{3,7}{1,39} = 2,65,$$

$$\alpha = \frac{i-1}{n-1} = \frac{2,65-1}{3-1} = 0,825.$$

2. 293° C da suvning bug' bosimi $p_{\text{H}_2\text{O}}^0 = 17,54$ mm sim. ust.ga teng. 2,21 g CaCl_2 ning 100 g suvdagi eritmasi bug' bosimi 17,41 mm sim. ust.ga teng. α ni aniqlang.

Yechish. α ning bug' bosimi bilan bevosita bog'langan tenglamasi yo'q. α faqat i bilan, i esa p bilan (VIII.4) tenglama orqali bog'langan. Demak, oldin i (VIII.4) tenglamadan topilgach, (VIII.6) tenglamadan topilganidan so'ng α aniqlanadi.

$$\frac{p^0 - p}{p^0} = \frac{in_2}{n_1 + n_2} \quad \text{va bundan} \quad i = \frac{(p^0 - p)(n_1 + n_2)}{p^0 \cdot n_2}$$

$$n_1, n_2 \text{ ni aniqlash: } M_{\text{CaCl}_2} = 111; \quad n_1 = \frac{2,21}{111} = 0,02; \quad n_2 = \frac{100}{18} = 5,55,$$

$$i = \frac{(p^0 - p)(n_1 + n_2)}{p^0 n_2} = \frac{(17,54 - 17,41)(5,55 + 0,02)}{17,54 \cdot 0,02} = 2.$$

$$\alpha = \frac{i-1}{n-1} = \frac{2-1}{3-1} = \frac{1}{2} = 0,5.$$

$$C_{\beta_-}^0 = -\frac{1,2 \cdot 10^{-4}}{2} + \sqrt{1,2 \cdot 10^{-4} \cdot 0,6} = 8,4 \cdot 10^{-3} \text{ ion} / \text{m}^3.$$

3. 298 K da 0 benzoy kislotaning dissotsilanish $\text{JC}_6\text{H}_4\text{COOH} \rightleftharpoons \text{H} + \text{JC}_6\text{H}_4^{\text{COO}}$ konstantasi $K_D = 1,4 \cdot 10^{-3}$ ga teng. 0 benzoy kislotaning 0,5 mol/m³ konsentratsiyali eritmasining dissotsilanish darajasi (α) qanchaga teng?

Yechish. K_D bilan α — bogʻlangan tenglama (VIII.10):

$$K_D = \frac{\alpha^2}{1-\alpha} - C_0. \text{ Tenglama } \alpha \text{ ga nisbatan yechilsa:}$$

$$\alpha^2 C_0 + K_D = 0, \text{ bundan:}$$

$$\alpha = \frac{K_D \pm \sqrt{K_D^2 + 4K_D C_0}}{2C_0} = -1,4 \cdot 10^{-3} + \sqrt{(1,4 \cdot 10^{-3})^2 + 1,4 \cdot 10^{-3} \cdot 0,5} =$$

$$= 5,13 \cdot 10^{-3} : (1,4 \cdot 10^{-3})^2 \ll 1,4 \cdot 10^{-3} \cdot 0,5$$

boʻlganligidan $(1,4 \cdot 10^{-3})^2$ hisobga olinmadi.

4. 1/200 H konsentratsiyali kislota eritmasining pH qiymatini aniqlang.

Yechish. (VIII. 11) tenglamaga muvofiq:

$$\text{pH} = -\lg[\text{H}^+] = -\lg(5 \cdot 10^{-3}) = -\lg 5 + 3 = 0,7 + 3 = 2,3.$$

5. Kislota pH 6,3 ga teng. Vodorod ionining konsentratsiyasini aniqlang.

Yechish. (VIII. 11) tenglamaga muvofiq:

$$[\text{H}^+] = 10^{-\text{pH}}; \quad \lg[\text{H}^+] = -6,3 = 7,7 = 5 \cdot 10^{-7}.$$

6. 0,1 n NH_4OH eritmasining $\text{pH} = 11,27$ ga, suv ionlarining koʻpaytmasi $K_b = 0,71 \cdot 10^{-14}$ ga teng. NH_4OH ning dissotsilanish konstantasi K_D ni aniqlang.

Yechish. (VIII. 10) tenglamaga muvofiq:

$$K_D = \frac{\alpha^2}{1-\alpha} C_0.$$

Demak, K_D qiymatini aniqlash uchun α ning qiymatini, pH va K_b qiymatlarini oʻzaro bogʻlagan tenglama (VIII.7) dan foydalaniladi:

$$\alpha = \frac{C}{C_0}; \quad \alpha = \frac{[\text{OH}^-]}{C_0}.$$

O'z navbatida, (OH^-) qiymati pH dan, ya'ni (H^+) qiymatidan foydalanib topiladi.

$$\text{pH} = -\lg[\text{H}^+]; [\text{H}^+] = 10^{-\text{pH}}; \lg[\text{H}^+] = -11,27 \text{ va } [\text{H}^+] = 1,86 \cdot 10^{-11};$$

$$[\text{OH}^-] = \frac{K_b}{[\text{H}^+]} = \frac{0,71 \cdot 10^{-14}}{1,86 \cdot 10^{-11}} = 3,82 \cdot 10^{-5}$$

va

$$\alpha = \frac{[\text{OH}^-]}{C_0} = \frac{3,82 \cdot 10^{-5}}{0,1} = 3,82 \cdot 10^{-4}.$$

Demak:

$$K_D = \frac{\alpha^2}{1-\alpha} C_0 = \frac{(3,82 \cdot 10^{-4})^2}{1-3,82 \cdot 10^{-4}} \cdot 0,1 = 1,459 \cdot 10^{-8}$$

$(1-3,82 \cdot 10^{-4} \approx 1 \text{ deb qabul qilindi}).$

7. 0,1 n sirka kislota va 0,1 n natriy asetatdan iborat bufer eritmaning pH qanchaga teng? Sirka kislotaning 25°C dagi dissotsilanish konstantasi $K_D = 1,86 \cdot 10^{-5}$.

Y e c h i s h . Bufer eritmalarida

$$[\text{H}^+] = K_K \frac{[\text{kislota}]}{[\text{tuz}]} = \frac{1,86 \cdot 10^{-5} \cdot 0,1}{0,1} = 1,86 \cdot 10^{-5}; \text{ pH} = 4,73.$$

Agar bu tenglamaga ko'ra kislotaning shu konsentratsiyadagi dissotsilanish darajasi e'tiborga olinsa, aniq javob olinadi. $\alpha = 0,79$.
Demak:

$$[H^+] = \frac{1,86 \cdot 10^{-5}}{0,79} : \frac{0,1}{0,1} = 2,36 \cdot 10^{-5} \quad \text{va } pH = 4,627.$$

Yechish: a) K_b ni aniqlaymiz, (VIII.15) tenglamaga muvofiq:

$$K_p = \frac{K_b}{K_k} = \frac{1,2 \cdot 10^{-14}}{1 \cdot 10^{-9}} = 1,2 \cdot 10^{-11},$$

b) β ni aniqlaymiz. (VIII.15) va (VIII.16) tenglamaga muvofiq:

$$K_p = \frac{\beta^2}{1-\beta} C_0 \quad 1 \gg \beta \quad \text{e'tiborga olinsa, } (1-\beta) \approx 1 \text{ bo'ladi.}$$

Demak:

$$K_p = \beta^2 C_0; \quad \beta = \sqrt{\frac{K_p}{C}} = \sqrt{\frac{1,2 \cdot 10^{-11}}{1 \cdot 10^{-3}}} = 1,2 \cdot 10^{-4},$$

d) muhit reaksiyasi pH ni aniqlaymiz. Buning uchun avval gidroksil ioni konsentratsiyasi va so'ngra vodorod ioni konsentratsiyasini va nihoyat pH ni aniqlaymiz:

$$[OH^-] = \beta C_0 = 1,26 \cdot 10^{-4} \cdot 10^{-3} = 1,26 \cdot 10^{-7};$$

$$[H^+] = \frac{K_b}{[OH^-]} = \frac{1,2 \cdot 10^{-14}}{1,2 \cdot 10^{-7}} = 1 \cdot 10^{-7}$$

va $pH = 7$.

8. $AgBO_3$ ning to'yingan eritmasida $t = 0,0081$ mol tuz bor. Bu eritmaga $0,0085$ mol $AgNO_3$ qo'shilgan. $AgBO_3$ ning $AgNO_3$ qo'shilgandan keyingi eruvchanligini aniqlang. $\alpha_{AgBO_3} = 1$ va $\alpha_{AgNO_3} = 1$ ga teng.

Yechish. (VIII. 13) ga muvofiq:

$$L_{\text{AgBO}_3} = [\text{Ag}^+] \cdot [\text{BO}_3^-] = n^2 = (0,0081)^2 = 6,55 \cdot 10^{-5}.$$

AgBO_3 ning AgNO_3 qo'shilgandagi eruvchanligi $C_1 = [\text{BO}_3^-]$;

$[\text{Ag}^+]$ konsentratsiyasi:

$$\left. \begin{array}{l} \text{AgBO}_3 \text{ dan hosil bo'lganda } C_1 \\ \text{AgNO}_3 \text{ dan hosil bo'lganda } C_2 \end{array} \right\} [\text{Ag}^+] = C_1 + C_2.$$

$$\text{Demak: } L_{\text{AgBO}_3} = (C_1 + C_2) C_1 = (0,0085 + C_1) C_1 = 6,55 \cdot 10^{-5},$$

bundan: $C_1 = 0,0049 \text{ mol/l} = 4,9 \cdot 10^{-3} \text{ mol/l}$.

9. 25°C da AgCl ning eruvchanligi $C_1 = 1,5 \cdot 10^{-5} \text{ mol/l}$. Shu haroratda AgBr ning eruvchanligi $C_2 = 7 \cdot 10^{-7} \text{ mol/l}$. Eritmada $[\text{Ag}^+]$ $[\text{Cl}^-]$, $[\text{Br}^-]$ konsentratsiyasini aniqlang.

Yechish.

$$L_{\text{AgCl}} = [\text{Ag}^+] [\text{Cl}^-] = (1,5 \cdot 10^{-5})^2 = 2,25 \cdot 10^{-10}.$$

$$L_{\text{AgBr}} = [\text{Ag}^+] [\text{Br}^-] = (7 \cdot 10^{-7})^2 = 4,9 \cdot 10^{-13}.$$

Eritmada kationlar konsentratsiyasi anionlar konsentratsiyasiga teng bo'lishi kerak:

$$[\text{Ag}^+] = [\text{Cl}^-] + [\text{Br}^-] \quad \text{yoki} \quad [\text{Br}^-] = [\text{Ag}^+] - [\text{Cl}^-]$$

Br ning miqdori AgBr ga qo'yilsa:

$$L_{\text{AgBr}} = [\text{Ag}^+] [\text{Br}^-] = [\text{Ag}^+] ([\text{Ag}^+] - [\text{Cl}^-]),$$

ikkinchi tomondan:

$$L_{\text{AgCl}} = [\text{Ag}^+] [\text{Cl}^-] = 2,25 \cdot 10^{-10} \text{ ga teng va } [\text{Cl}^-] = \frac{2,25 \cdot 10^{-10}}{[\text{Ag}^]}.$$

Cl^- ionining bu qiymati yuqoridagi AgBr tenglamaga qo'yilsa:

$$L_{\text{AgBr}} = [\text{Ag}^+][\text{Br}^-] = \{[\text{Ag}^+] - [\text{Cl}^-]\} = [\text{Ag}^+]\{[\text{Ag}^+]\} - \frac{2,25 \cdot 10^{-10}}{[\text{Ag}^+]} = 4,9 \cdot 10^{-13}.$$

Bundan:

$$[\text{Ag}^+] = \sqrt{L_{\text{AgCl}} + L_{\text{AgBr}}} = \sqrt{2,25 \cdot 10^{-10} + 4,9 \cdot 10^{-13}} = 1,502 \cdot 10^{-5}$$

va

$$[\text{Br}^-] L_{\text{AgBr}} = 4,9 \cdot 10^{-13} \text{ bo'lganligidan:}$$

$$[\text{Br}^-] = \frac{4,9 \cdot 10^{-13}}{1,502 \cdot 10^{-5}} = 3,21 \cdot 10^{-8}.$$

10. 0,01 n KCl eritmasining solishtirma qarshiligi $\rho = 709,22 \Omega^{-1} \cdot \text{sm}$. Solishtirma va ekvivalent elektr o'tkazuvchanlikni aniqlang. Yechish. (VIII. 15) tenglamaga muvofiq:

$$\lambda_c = \frac{1}{\rho} = \frac{1}{709,22} = 1,41 \cdot 10^{-3} \Omega^{-1} \cdot \text{sm}^{-1} = 0,141 \Omega^{-1} \cdot \text{sm}^{-1}.$$

λ_c ni (VIII. 17) tenglamadan foydalanib topiladi:

$$\lambda_c = \frac{\lambda_c}{c} = \frac{0,141}{0,01} = 0,141 \cdot 10^2 \Omega^{-1} \cdot \text{kg} \cdot \text{ekv} \cdot \text{m}^2.$$

11. 25°C da cheksiz suyultirilgandagi elektr o'tkazuvchanlik $\lambda_\infty = 42,8 \Omega^{-1} \cdot \text{kg} \cdot \text{ekv} / \text{m}^2$. Dissotsilanish konstantasi $K = 7,9 \cdot 10^{-10} \times 0,2 \text{ kg} \cdot \text{ekv} / \text{m}^3$ konsentratsiyali HCN eritmasining solishtirma o'tkazuvchanligi qanchaga teng?

Yechish. (VIII. 17) tenglamaga muvofiq $\lambda_s = C \lambda_c$. Demak, avval λ_c ni aniqlash kerak. Eritma konsentratsiyasi va dissotsilanish

konstantasi bilan bog'langan tenglama Ostvaldning suyultirish qonuniga tegishli. Berilgan ma'lumotlardan foydalanib (VIII. 28) tenglama bilan λ_e va λ_s ni aniqlash kerak:

$$K_D = \frac{\lambda_e^2 C_0}{\lambda_\infty (\lambda_\infty - \lambda_e)},$$

bu tenglama λ_e ga nisbatan yechilsa:

$$\lambda_e = \frac{-\lambda_\infty \pm \sqrt{\lambda_\infty^2 - 4\lambda_\infty^2 - K_D C_0}}{2C_0} \sim \frac{\lambda_\infty}{2C_0} (-1 \pm \sqrt{1 + K_D C})$$

λ_e noldan kichik bo'lishi mumkin emasligidan:

$$\begin{aligned} \lambda_e &= \frac{\lambda_\infty}{2C_0} (\sqrt{1 + 4K_D C} - 1) = \frac{42,8}{2} \sqrt{1 + 4 \cdot 7,9 \cdot 10^{-10} \cdot 0,2} - 1 \approx \\ &\approx 6,8 \cdot 10^{-9} \Omega^{-1} \cdot \text{m}^{-1}. \end{aligned}$$

12. 291 K da 0,1 n sirka kislota (CH_3COOH) ning solishtirma elektr o'tkazuvchanligi $\lambda_e = 4,7 \cdot 10^{-4} \Omega^{-1}$ ga, 0,001 n natriy asetat CH_3COONa niki esa $\lambda_e = 7,81 \cdot 10^{-5} \Omega^{-1}$ ga teng. Vodorod ionining harakatchanligi $\lambda_{+,H^+} = 348,82$ ga, natriy ioniniki $\lambda_{+,Na^+} = 50,11$ ga teng. 291 K da sirka kislota ning dissotsilanish konstantasi qanchaga teng?

Y e c h i s h . (VIII. 10) tenglamaga muvofiq:

$$K_D = \frac{\alpha^2}{1 - \alpha} C_0.$$

Demak, masalani yechish uchun α ni topish kerak. O'z navbatida,

$$\alpha = \frac{\lambda_e}{\lambda_\infty} \text{ teng. } \lambda_e \text{ ni } \lambda_c \text{ dan, ya'ni } \lambda_e = \lambda_c C \text{ tenglamadan, } \lambda_\infty \text{ ni esa}$$

Kolraush qonunidan, $\lambda_\infty = \lambda_+ + \lambda_-$ dan foydalanib aniqlash kerak bo'ladi. Lekin $\lambda_\infty = \lambda_{+,H^+} + \lambda_{-,CH_3COO^-}$ bo'lganligidan avval

λ_{-,CH_3COO^-} ni aniqlab olish kerak. Shu amallarni oxiridan boshlab bajarish kerak:

$$\lambda_{c,CH_3COOH} = \frac{\lambda_c \cdot 1000}{c} = \frac{4,7 \cdot 10^{-4}}{0,1} = 4,7 \cdot 10^{-3} \Omega^{-1} \cdot \text{sm}^{-2} = 4,7 \Omega^{-1} \cdot \text{m}^{-2}.$$

λ_{-,CH_3COO^-} ni aniqlaymiz. CH_3COONa eritmasi juda suyultirilganligidan amaliy $\lambda_\infty = \lambda_c$.

$$\lambda_{\infty,CH_3COONa} = \lambda_{+,Na} + \lambda_{-,CH_3COO^-}$$

$$\lambda_{-,CH_3COO^-} = \frac{\lambda_{\infty,CH_3COONa}}{\lambda_{+,Na}} = 33,7 \Omega^{-1} \cdot \text{m}^{-2}$$

va

$$\lambda_{\infty,CH_3COOH} = \lambda_{+,H^+} + \lambda_{-,CH_3COO^-} = 349,82 + 33,7 = 383,2.$$

Demak;

$$\alpha = \frac{\lambda_e}{\lambda_\infty} = \frac{4,71}{383,2} = 0,0212;$$

$$K_D = \frac{\alpha^2 C_0}{1-\alpha} = \frac{(0,0212)^2 0,1}{1-0,0212} = 4,9 \cdot 10^{-4}.$$

13. 298 K da AgBr ning solishtirma elektr o'tkazuvchanligi $\lambda_s = 1,576 \cdot 10^{-6} \Omega^{-1} \cdot \text{sm}^2$ ga teng. Suvning solishtirma elektr o'tkazuvchanligi $\lambda_{\text{C}, \text{H}_2\text{O}} = 1,519 \cdot 10^{-6} \Omega^{-1} \cdot \text{sm}^2$ ga teng. Quyidagi tuzlarning ekvivalent elektr o'tkazuvchanligi $\lambda_{\text{c}, \text{KBr}} = 137,8$, $\lambda_{\text{c}, \text{KNO}_3} = 131,3$, $\lambda_{\text{c}, \text{AgNO}_3} = 127,1 \Omega^{-1} \cdot \text{sm}^2$. Hamma tuzlar to'liq dissotsilangan, $a = 1 \cdot \text{Ag}^+$ ionning eruvchanligi va AgBr eruvchanlik ko'paytmasini aniqlang.

Yechish. $\alpha = 1$ bo'lganligidan $\lambda_c = \lambda_\infty$ va (VIII. 18) tenglama Kolraush qonuniga muvofiq:

$$a) \lambda_{\infty, \text{AgNO}_3} = \lambda_{+, \text{Ag}^+} + \lambda_{-, \text{NO}_3^-};$$

$$b) \lambda_{\infty, \text{KNO}_3} = \lambda_{+, \text{K}^+} + \lambda_{-, \text{NO}_3^-};$$

$$d) \lambda_{\infty, \text{KBr}} = \lambda_{+, \text{K}^+} + \lambda_{-, \text{Br}^-}.$$

a va b tenglama yig'indisidan « d » tenglama olinsa:

$$\lambda_{\infty, \text{AgBr}} = \lambda_{\infty, \text{AgNO}_3} + \lambda_{\infty, \text{KBr}} - \lambda_{\infty, \text{KNO}_3} = 127,1 + 137,8 - 131,3 = 133,6 \Omega^{-1} \cdot \text{sm}^2,$$

ikkinchi tomondan eruvchanlik C :

$$\lambda_c = \lambda_\infty = \frac{\lambda_c}{C} \quad \text{va} \quad C = \frac{\lambda_c}{\lambda_\infty} = 4,49 \cdot 10^{-7} \text{ g-ekv/l.}$$

va

$$L_{\text{AgBr}} = [\text{Ag}^+][\text{Br}^-] = (4,49 \cdot 10^{-7})^2 = 2,03 \cdot 10^{-13}.$$

14. 0,1784% NaCl eritmasi elektroliz qilingandan so'ng anod uchastkada 226,69 g eritmada 0,04679 g Cl_2 borligi, katod uchastkada 331,4 g eritmada 0,05302 g Cl_2 borligi aniqlangan. Ionlarning tashish soni (n_{Na^+} , n_{Cl^-})ni aniqlang.

Y e c h i s h . (VIII.20) tenglamadan foydalanib, anod va katod uchastkalarida konsentratsiyaning o'zgarishini aniqlash kerak. Elektrolizdan so'ng:

anodda $226,69 - 0,04679 = 226,64$ g suv bor,

katodda $331,4 - 0,0530 = 331,34$ g suv bor.

Elektrolizdan oldin eritmada $100 - 0,1784 = 99,82$ g suv bor edi, anodda esa:

$$\left. \begin{array}{l} 99,82 - 0,1784 \\ 226,64 - x \end{array} \right\} \text{Cl}_2 = \frac{226,64 \cdot 0,1784}{99,8^2} = 0,405 \text{ g Cl}_2$$

katodda:

$$\left. \begin{array}{l} 99,82 - 0,1784 \\ 331,4 - x \end{array} \right\} \text{Cl}_2 = \frac{331,4 \cdot 0,1784}{99,82} = 0,592 \text{ g Cl}_2$$

$$\Delta p_k = 0,592 - 0,05302 = 0,5389$$

$$\Delta p_a = 0,405 - 0,04679 = 0,3582$$

$$\Delta p_k = \Delta p_a = 0,8971$$

va

$$n_{\text{Cl}^-} = \frac{0,5389}{0,8971} = 0,601$$

$$n_{\text{Na}^+} = 1 - n_{\text{Cl}^-} = 0,399.$$

15. Natriy asetat CH_3COONa eritmasida $\lambda_x = 82 \text{ } \Omega^{-1} \cdot \text{sm}^2$, kaliy asetat CH_3COOK eritmasiniki $\lambda_x = 140,8 \text{ } \Omega^{-1} \cdot \text{sm}^2$ ga teng,

$n_{\text{CH}_3\text{COO}^-} = 0,4$, $n_k = 0,50$ ga teng. Kaliy asetat eritmasining cheksiz suyultirilgan eritmadagi o'tkazuvchanligi λ_∞ ni aniqlang.

Yechish. (VIII. 18) tenglamaga muvofiq:

$\lambda_{\infty, \text{CH}_3\text{COOK}} = \lambda_{+, \text{K}} + \lambda_{-, \text{CH}_3\text{COO}^-}$ harakatchanlik λ_+ , λ_- va tashish son n_+ , n_- larining o'zaro bog'langan tenglamasidan foydalaniлади:

$$\lambda_+ = n_+ \lambda_{\infty}; \quad \lambda_- = n_- \lambda_{\infty}$$

$$\lambda_{+, \text{K}^+} = 0,50 \cdot 140,8 = 70,4 \Omega^{-1} \cdot \text{sm}^2$$

$$\lambda_{-, \text{CH}_3\text{COO}^-} = 0,4 \cdot 82 = 32,8 \Omega^{-1} \cdot \text{sm}^2$$

$$\lambda_{\infty, \text{CH}_3\text{COOK}} = 32,8 + 70,4 = 103,2 \Omega^{-1} \cdot \text{sm}^2$$

MASALALAR

1. 291 K da $C_1 = 0,8718 \text{ kmol/m}^3$ konsentratsiyadagi qandning suvdagi eritmasining osmotik bosimi P_q , $C_2 = 0,5 \text{ kmol/m}^3$ konsentratsiyadagi NaCl ning suvdagi eritmasi osmotik bosimi P_{NaCl} ga teng. NaCl ning dissotsilanish darajasi α ni aniqlang.

2. CaCl_2 ning 7,5% suvdagi eritmasi 1 atm.da $T_k = 347 \text{ K}$ da qaynaydi. Suvning bug' bosimi 347 K da 787 mm ga teng. Izotonik koeffitsiyent « i » ni aniqlang.

3. C molar konsentratsiyali glitserinning osmotik bosimi P_g va NaNO_3 ning $C_2 = 8,49 \text{ g/100 g H}_2\text{O}$ eritmasining osmotik bosimi P_l ga teng. NaNO_3 eritmasida $\alpha = 0,640$ ga teng. Glitserinning konsentratsiyasini aniqlang.

4. 11,74 g NaCl ning 200 g suvdagi eritmasida $\alpha = 0,70$ ga teng. Eritmaning muzlash harorati va uning pasayishi ΔT_m ni aniqlang.

5. 0,1 mol tuzning 100 g suvdagi eritmasi $t_m = -0,054^\circ \text{C}$ da muzlaydi. $\alpha = 0,72$. Bu tuz dissotsilanganda qancha ion (n) hosil bo'ladi?

6. MgCl_2 tuzi eritmasining tajribada topilgan muzlash harorati $t_m = -3,7^\circ \text{C}$, dissotsilanish darajasi $\alpha = 0,825$. Suvning krioskopik doimiysi 1,86. Eritmalar tarkibini aniqlang. 300 g suvda necha gramm MgCl_2 tuzi erigan?

7. 298 K da 0 yodbenzoy kislotaning dissotsilanish konstantasi $K_d = 1,4 \cdot 10^{-3}$ ga teng. 0,5 kg $\cdot$ ion/ m^3 eritmada dissotsilanish darajasi α nimaga teng?

8. Bromid etilaminning $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$ 0,05 kmol/ m^3 eritmasida (ya'ni $\lg K_b$) $\text{p}K_d = 3,662$. Izotonik koeffitsiyent « i » ni aniqlang.

9. Aluminiy xloridning suvdagi 0,05% li eritmasida $\alpha = 1$ ga teng. Uni ideal eritma deb qabul qilib, eritma ustida suv bug'ining nisbiy kamayishi $\frac{\rho^0 - \rho}{\rho^0}$ ni aniqlang.

10. 298 K da ammoniy gidroksid NH_4OH ning 0,1 m eritmasida $K_d = 1,77 \cdot 10^{-5}$ ga teng. H^+ , OH^- ionlarining konsentratsiyasini aniqlang.

11. Eritmalarning $\text{pH} = 4,70$ va $\text{pH} = 12,5$ ga teng. Eritmalardagi (H^+) va (OH^-) miqdori qanchaga teng? $K_b = 1,2 \cdot 10^{-14}$.

12. 0,1 n NH_4OH eritmasining $\text{pH} = 11,27$ ga teng. Suv ionlarining ko'paytmasi $K_b = 0,71 \cdot 10^{-14}$. NH_4OH ning dissotsilanish konstantasini aniqlang.

13. $\frac{1}{400}$ n HCl kislotaning, $\frac{1}{500}$ n HCl kislotaning pH ini aniqlang.

14. $\frac{1}{200}$ n NaOH eritmasining pH ini aniqlang. Suv ionlarining ko'paytmasi $K_w = 1,2 \cdot 10^{-14}$.

15. 298 K da ammoniy gidroksid NH_4OH ning dissotsilanish konstantasi $K_d = 1,77 \cdot 10^{-5}$ ga teng. 0,1 mol eritmasining $[\text{H}^+]$, $[\text{OH}^-]$ va pH ini aniqlang. Suv ionlari ko'paytmasi $K_b = 1,008 \cdot 10^{-14}$ ga teng.

16. AgBO_3 ning to'yingan eritmasida $m = 0,0081$ mol tuz bor. Bu eritmaga $m = 0,0085$ mol AgNO_3 qo'shilgan. $L_{\text{AgNO}_3} = L_{\text{AgBO}_3} = 1$ teng. AgBO_3 ning shu eritmadagi eruvchanligini aniqlang.

17. 298 K da CuCl ning suvda va 0,025 m MgSO_4 eritmasidagi eruvchanligini aniqlang. CuCl ning eruvchanlik ko'paytmasi $L = 3,2 \cdot 10^{-7}$ ga teng.

18. 25° C da AgBr ning 0,001 molal KBr eritmasidagi eruvchanlik ko'paytmasini aniqlang.

19. Yuzasi 5 sm^2 bo'lgan va bir-biridan 2 sm masofada joylashgan ikki elektrod orasi 0,05 n KNO_3 eritmasi bilan to'ldirilgan. 0,05 n KNO_3 ning ekvivalent elektr o'tkazuvchanligi $\lambda_e = 109 \text{ sm}^3 \Omega^{-1} \text{ g-ekv}^{-1}$ ga teng. Solishtirma elektr o'tkazuvchanlikni aniqlang.

20. Yuzasi 4 sm^2 bo'lgan va 0,7 sm masofada joylashgan 2 elektrod orasidagi hajm 0,1 mol CuSO_4 bilan to'ldirilgan. Eritma qavatining qarshiligi 23 Ω . Solishtirma va ekvivalent elektr o'tkazuvchanlikni aniqlang.

21. Yuzasi 2 sm^2 va 5 sm oraliqda joylashgan 2 elektrod orasidagi hajmga 1 mol AgNO_3 eritmasi to'ldirilgan. $\lambda_e = 94,3 \Omega^{-1} \cdot \text{sm}^2/\text{g-ekv}^{-1}$. Solishtirma elektr o'tkazuvchanlikni aniqlang.

22. Sirka kislotaning dissotsilanish konstantasi $K_D = 1,76 \cdot 10^{-5}$ ga teng, $\lambda_\infty = 390,7$ ga teng. 0,1 n sirka kislota eritmasining ekvivalent elektr o'tkazuvchanligi va vodorod ionlarining konsentratsiyasini aniqlang.

23. 25° C da kaliy nitrat eritmasini cheksiz suyultirilgandagi elektr o'tkazuvchanlik 103,97 $\Omega^{-1} \cdot \text{sm}^2 \text{ g-ekv}$. Kaliy ionining harakatchanligi 73,58 $\Omega^{-1} \cdot \text{sm}^2 \text{ g-ekv}^{-1}$. Nitrat ionining

harakatchanligini va cheksiz suyultirilgan eritmada tashish sonini aniqlang.

24. KCl eritmasining $\lambda_{\infty} = 130,1 \Omega^{-1} \cdot \text{sm}^2 \text{g-ekv}^{-1}$ ga teng. Cl^- ionining tashish soni 0,5 ga teng. K^+ va Cl^- ionlarining harakatchanligini aniqlang.

25. Yog' kislotasi $\text{C}_3\text{H}_7\text{COOH}$ ning dissotsilanish konstantasi $K_d = 1,54 \cdot 10^{-5}$. Kislotada 2048 l/g-ekv gacha suyultirilgan. Vodorod ioni konsentratsiyasini va ekvivalent elektr o'tkazuvchanlikni aniqlang.

26. Yacheyka hajmi solishtirma elektr o'tkazuvchanligi $5,8 \cdot 10^{-3}$ bo'lgan KCl eritmasi bilan to'ldirilganda elektr qarshilik 103,0 Ω bo'lgan. Shu yacheykani 0,01 n sirka kislotasi bilan to'ldirilganda 5770 Ω bo'lgan. 0,01 n sirka kislotaning ekvivalent elektr o'tkazuvchanligini aniqlang.

27. Suyultirilgan SrCl_2 eritmasida Sr^{2+} va Cl^- ionlarining mutlaq tezliklari $5,2 \cdot 10^{-3}$ va $6,8 \cdot 10^{-3}$ m/sek. Eritmaning ekvivalent elektr o'tkazuvchanligi, ionlarning harakatchanligini va ionlarning tashish sonini aniqlang.

28. KCeO_4 ning cheksiz suyultirilgan eritmasida $\lambda_{\infty} = 122,8 \Omega^{-1} \cdot 1 \text{ sm}^2 \text{g-ekv}^{-1}$. ClO_4 ning tashish soni 0,481. K^+ va ClO_4 ionlarining harakatchanligini aniqlang.

29. Cu va Pt elektrodli idishda 41,59 eritmada 1 g CuSO_4 tutgan eritma elektroliz qilingan. Elektrolizdan so'ng katod maydonida 54,706 g, eritmada esa 0,5118 g CuO bo'lgan. Tashish sonlari n_+ , n_- ni aniqlang.

30. Cd va Pt elektrodli idishda 0,201% CdCl_2 eritmasi elektroliz qilingan. Elektrolizdan so'ng anod maydonida 53,59 g eritmada 0,0802 g Cl_2 , katod maydonida 54,12 g eritmada 0,0966 g Cl_2 bo'lgan. Ionlarning tashish sonini aniqlang.

31. Monoxlor sirka kislotaning CH_3ClCOOH dissotsilanish konstantasi 298 K da $1,55 \cdot 10^{-3} \text{ mol/l}$. $V = 32 \text{ l/mol}$ suyultirishda ekvivalent elektr o'tkazuvchanligi $77,2 \Omega^{-1} \cdot \text{sm}^2 \text{g-ekv}^{-1}$ ga teng. Monoxlor sirka kislotaning cheksiz suyultirilgandagi elektr o'tkazuvchanligi λ_{∞} ni aniqlang.

32. 298 K da $1,59 \cdot 10^{-4}$ m sirka kislotaning $\lambda_c = 109,78 \Omega^{-1} \cdot \text{sm}^2 \text{ g-ekv}^{-1}$ ga teng. Ionlarning harakatchanligi $\lambda_{+,H^+} = 349,80 \Omega^{-1} \cdot \text{sm}^2$ va $\lambda_{-,CH_3COO^-} = 40,9 \Omega^{-1} \cdot \text{sm}^2$ ga teng. Eritmaning pH ini va dissotsilanish konstantasini aniqlang.

KO'P VARIANTLI MASALALAR

A moddaning: a) solishtirma va ekvivalent elektr o'tkazuvchanliklarini suyultirish bilan o'zgarishini ifoda qilgan grafikni chizing va b) ekvivalent elektr o'tkazuvchanlikning critma konsentratsiyasi bilan o'zgarishidan foydalanib λ_∞ qiymatini aniqlang.

Ish varianti	1	2	3	4	5	6	7	8	9
<i>A</i> modda	HCN	HNO ₂	HClO	HCOOH	CH ₃ COOH	(CH ₃) ₂ AsOOH	C ₆ H ₅ OH	C ₆ H ₅ COOH	NH ₄ OH

1. 298 K da *A* modda critmasining solishtirma qarshiligi konsentratsiya bilan o'zgarishini aniqlang.

<i>C</i> mol/l	<i>A</i> modda uchun $r \cdot \Omega \cdot \text{sm}$								
	HCN	HNO ₂	HClO	HCOOH	CH ₃ COOH	CH ₃ AsOH	C ₆ H ₅ OH	C ₆ H ₅ COOH	NH ₄ OH
0,1	$3,10 \times 10^3$	4,32	927	6,05	19,6	131	$7,46 \times 10^3$	9,75	2,53
0,05	$4,37 \times 10^3$	5,7	1390	8,91	27,6	180	1080×10^3	14,1	10,3
0,03	$5,84 \times 10^3$	7,5	1810	10,3	34,8	235	$14,50 \times 10^3$	18,5	14,5
0,01	$10,1 \times 10^3$	13,4	3120	18,2	61,0	402	$23,5 \times 10^3$	31,4	25,8
0,005	$14,3 \times 10^3$	20,4	4360	25,9	87,0	582	$41,50 \times 10^3$	48,8	100
0,003	$18,3 \times 10^3$	20,8	5560	35,8	103	706	$52,7 \times 10^3$	57,9	143
0,001	$31,9 \times 10^3$	52,7	10000	68,5	185	1310	$74,60 \times 10^3$	113,0	251

2. 298 K da quyidagi moddalar uchun λ_{∞} dan foydalanib molar elektr o'tkazuvchanlik (λ_m) qiymatini aniqlang.

Modda	$\lambda_{\infty} \times 10^2 \Omega^{-1} \cdot \text{sm}^2 \text{ g-ekv}^{-1}$	Modda	$\lambda_{\infty} \times 10^2 \Omega^{-1} \cdot \text{sm}^2 \text{ g-ekv}^{-1}$
AgCNS	1,283	La ₂ (SO ₄) ₃	1,50
Ag ₂ SO ₄	1,419	MgBr ₂	1,31
BaCl ₂	1,40	Mg(BrO ₃) ₂	1,08
CaCl ₂	1,30	MgCl ₂	1,29
LaCl ₃	1,40	Mg(CNS) ₂	1,19
La(CNS) ₃	1,36	MgF ₂	1,08
La(JO ₃) ₃	1,10	MgJ ₂	1,30
MgSO ₄	1,33	SrCl ₂	1,36
PbCl ₂	1,46	TiNO ₃	1,51
PbC ₂ O ₄	1,43	Ti ₂ SO ₄	1,55
Pb(CNS) ₂	1,36		
PbSO ₄	1,10		

3. Quyidagi jadvalda 298 K da yomon eruvchi *A* modda uchun solishtirma qarshiligi ρ berilgan. Shu haroratda suvning solishtirma qarshiligi $\rho_{\text{H}_2\text{O}} = 1 \cdot 10^{-4} \Omega \cdot \text{sm}$. Quyidagi kattaliklarning qiymatini aniqlang: 1) *A* moddaning toza suvdagi eruvchanligi; 2) *A* moddaning eruvchanlik ko'paytmasi (eritma kuchli suyultirilganligidan $\gamma_{\pm} \approx 1$); 3) 0,01 mol *P* modda tutgan eritmada *A* moddaning eruvchanligi; 4) 0,01 mol *C* modda tutgan eritmada *A* moddaning eruvchanligi; *A*, *B*, *C* moddalar to'la dissotsilangan.

Variantlar	$\rho \times 10^{-4} \Omega \cdot \text{sm}$	Moddalar		
		<i>A</i>	<i>B</i>	<i>C</i>
1	0,0141	SrCrO ₄	H ₂ C ₂ H ₄	Na ₂ SO ₄
2	0,333	AgCl	HCl	Na ₂ SO ₄
3	0,055	AgJO ₃	HJO ₃	Na ₂ SO ₄
4	0,380	BaSO ₄	Na ₂ SO ₄	KBr
5	0,0038	TiBr	KBr	Na ₂ SO ₄
6	0,0248	PbSO ₄	LiSO ₄	KBr

4. Molal konsentratsiya (m) va o'rtacha ion aktivlik koeffitsiyentidan ($\gamma^{\pm}$) foydalanib, A moddaning o'rtacha ion konsentratsiyasi $C_{\pm}$, o'rtacha ion aktivlik $a_{\pm}$, o'rtacha molal aktivlik a ni aniqlang.

Variant-lar	A modda	m , mol/100	$g\pm$	Variant-lar	A modda	m , mol/100	$g\pm$
1	CaCl_2	1	0,500	14	$\text{Th}(\text{NO}_3)_4$	4,5	0,722
2	$\text{Ca}(\text{NO}_3)_2$	2	0,347	15	$\text{Cd}(\text{ClO}_4)_2$	5,5	0,413
3	MgJ_2	3	7,81	16	$\text{K}_3\text{Fe}(\text{CN})_6$	1	0,128
4	MgBr_2	4	12	17	ZnJ_2	2	1,012
5	$\text{Sr}(\text{ClO}_4)_2$	5	10,00	18	$\text{Cr}_2(\text{SO}_4)_3$	0,3	0,0238
6	CoJ_2	6	1,99	19	$\text{Th}(\text{NO}_3)_4$	0,4	0,192
7	LiCl	7	4,37	20	$\text{Ba}(\text{ClO}_4)_2$	5	2,3
8	HClO_4	8	11,83	21	$\text{Al}_2(\text{SO}_4)_2$	0,6	0,044
9	LiBr	9	12,92	22	$\text{K}_4\text{Fe}(\text{CN})_6$	0,7	0,051
10	NaOH	10	3,46	23	Na_2HPO_4	0,8	0,217
11	AlCl_3	0,5	0,331	24	KHAsO_4	0,9	0,301
12	LaCl_3	1,5	0,515	25	H_2SO_4	10	0,559
13	SnJ_2	3,5	1,504				

5. Quyida ionlarning harakatchanligi qiymati keltirilgan ma'lumotlardan foydalanib A moddaning $6 \cdot 10^{-3}$ mol/l eritmasining: 1) dissotsilanish darajasi α ni; 2) H ionining konsentratsiyasini va 3) pH ni aniqlang. λ ning qiymatini Ostvaldning suyultirish qonunidan foydalanib aniqlash mumkin.

Variant	1	2	3	4	5	6
A mod-dalar	izo- C_3H_7COOH	$H-C_3H_7$ $COOH$	$HCOOH$	C_2H_5COOH	CH_3COOH	NH_4OH

Ionlarning harakatchanligi (λ_+ , λ_-) $\Omega^{-1} \cdot \text{sm}^2 \cdot \text{mol}^{-1}$.

$H^+ - 349,8$

$HCOO^- - 54$

$CH_3COO^- - 40,9$

$C_2H_5COO^- - 35,8$

$C_3H_7COO^- - 34,2$

$NH_4^+ - 73,7$

$OH^- - 197,6$

IX bob

ELEKTR YURITUVCHI KUCH (EYuK) VA ELEKTROD POTENSIALLAR

Elektr yurituvchi kuch (EYuK) — elektr oqimini yuzaga keltiruvchi va elektr oqimining uzluksizligini ta'minlovchi qudratli omil — kuch (energiya)dir. Ko'pincha bu qudrat kimyoviy reaksiya energiyasi hisobiga yuz beradi. Kimyoviy reaksiya energiyasini elektr energiyasiga aylantirib beruvchi qurilma **galvanik element** deb ataladi. Odatda, bu qurilma elektrolit eritmalarga tushirilgan ikki elektroddan iborat bo'ladi. Elektrod eritma chegarasida potensial (elektr potensial) vujudga keladi.

Elektrolit eritmaga tushirilgan metall (yoki metallmas)dan hosil bo'lgan sistemaga **elektrod** deyiladi. Elektrodlar birinchi va ikkinchi tur xil bo'ladi. Birinchi xil elektrodlarda elektrod bilan eritma o'rtasida kation almashinishi, ikki xil elektrodlarda esa anion almashinish sodir bo'ladi. Elektrod bilan eritma o'rtasida boradigan ionlar almashinuvi natijasida elektrod va eritma chegarasida elektr potentsiali (π) vujudga keladi. Vujudga kelgan potensial elektrod xossasidan tashqari eritma konsentratsiyasiga bog'liq bo'lib, bu bog'lanish Nernst tenglamasida ifoda qilingan:

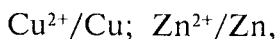
$$\pi = \pi^0 + \frac{RT \cdot \ln a_{M^+}}{zF}; \quad \pi^0 = \pi - \frac{RT}{zF} \ln a_M, \quad (\text{IX.1})$$

bunda: a — termodinamik aktivlik; F — Faradey soni; z — reaksiyada ishtirok qilgan elektronlar soni (valentlikning o'zgarishi); M^+ — metall va M^- — nometall ion.

Agar $a = 1$ bo'lsa, $\ln a = 0$ bo'ladi va (IX. 1) tenglamadan $\pi = \pi^0$ ni hosil qilamiz.

Demak, π^0 — eritmada ionlarning termodinamik aktivligi 1 ga teng bo'lganda vujudga kelgan potensial bo'lib, **normal** yoki **standart potentsial** deb ataladi. Turli elektrodning standart potentsiali ma'lumotnomalarda berilgan.

Birinchi xil elektrod(larga quyidagi elektrod(lar kiradi:
a) o'z ionini tutgan eritmaga tushirilgan metall elektrod:



bunda Zn^{2+}/Zn — sirt chegarasi ma'nosini bildiradi. Cu^{2+}/Cu — mis ion(lari bo'lgan (masalan, CuSO_4 eritmasi) eritmaga tushirilgan mis tayoqchasini (plastinka yoki simi) ifodalaydi.

b) **amalgama elektrod:** $\text{M}^{z+}/\text{M}(\text{Hg})$

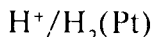
Amalgama elektrod:

$\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ misol bo'ladi. Uning potentsiali quyidagiga teng:

$$\pi = \pi^0 + \frac{RT}{zF} \ln \frac{a_{\text{cd}^{2+}}}{a_{\text{cd}}},$$

π^0 — amalgamadagi va eritmada kadmiyning aktivliklari ($a_{\text{cd}^{2+}} = 1$) yoki ular o'zaro teng bo'lgandagi standart amalgama elektrod potentsiali.

d) **gaz elektrod**, masalan, vodorod elektrod — Pt yuzasiga vodorod H_2 adsorbilangan va u H^+ ion tutgan eritmaga tushirilgan:



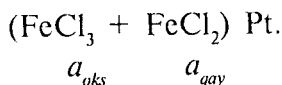
$$P = 1 \text{ atm.}$$

va quyidagi reaksiya boradi: $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\bar{e}$

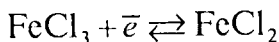
$$\text{va} \quad \pi = \pi^0 + \frac{RT}{F} \ln a_{\text{H}^+}. \quad (\text{IX.2})$$

π^0 — eritmada vodorod ionining termodinamik aktivligi 1 ga teng bo'lib, eritmaga 1 atmosfera bosim ostida vodorod yuborilganda hosil bo'ladigan potensial. Bu normal vodorod potentsiali etalon sifatida qabul qilinib, qiymati shartli ravishda nolga teng ($\pi^0 = 0$) deb qabul qilingan. Boshqa hamma elektrod potentsiallari qiymati shu normal vodorod potentsialiga nisbatan o'lchanadi.

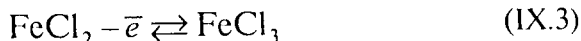
e) **oksidlanish-qaytarilish potentsiali (elektrodi)**. Bir vaqtda oksidlovchi va qaytaruvchi birikma tutgan eritmaga ($\text{FeCl}_3 + \text{FeCl}_2$) betaraf metall (masalan, Pt) tushiriladi:



Bu elektrodda quyidagi reaksiya boradi:



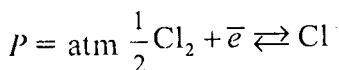
yoki



va

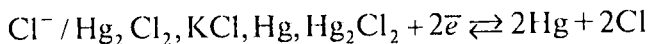
$$\pi = \pi^0 + \frac{RT}{zF} \ln \frac{a_{oks}}{a_{qay}}. \quad (\text{IX.4})$$

Ikkinchi xil elektrodga quyidagi elektrodlar kiradi: a) **gaz elektrod:** $\text{Cl}^- / \text{Cl}_2$, quyidagi reaksiya boradi:



$$\pi = \pi^0 + \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}}{a_{\text{Cl}_2}^{1/2}}$$

b) **kalomel elektrod:**

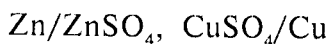


$$\pi = \pi^0 + \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (\text{IX.5})$$

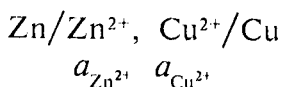
Turli elektrod potensiallarni o'lchashda vodorod elektrod noqulay bo'lganligidan, uning o'rniga etalon elektrod sifatida kalomel elektrod qo'llanadi. Kalomel elektrodning potentsiali vodorod elektrodga nisbatan aniq o'lchangan va u KCl eritmasi konsentratsiyasiga bog'liq bo'lib, 298 K da 0,1 n, KCl da 0,3365 V, 1,0 n eritmada +0,28228 V, to'yingan eritmada +0,2432 V ga teng.

Diffuzion potentsial. Bu kation va anionlarning harakatchanligi (elektr tashishi) turlicha bo'lishi sababli ikki xil eritma yo turli konsentratsiyali bir xil eritmalar chegarasida hosil bo'ladigan potentsialdir. Odatda, bu potentsial yo'qotiladi. Buning uchun ikki eritma bir-biri bilan tuz ko'prigi deb atalgan tuz to'ldirilgan naycha orqali birlashtiriladi. Tuz ko'prigi sifatida kation va anion ionlari harakatchanligi (yaqin) bo'lgan tuzlar olinadi (KCl , NH_4NO_3 va hokazo). Tuz ko'prigi yordamida diffuzion potentsialni amaliy yo'qotish mumkin.

Galvanik elementlar. Ikki elektrod birlashtirilganda galvanik element hosil bo'ladi va elektr yurituvchi kuch (EYuK) vujudga keladi. Masalan, mis-rux elektrodan iborat galvanik element quyidagicha tuzilgan bo'ladi:



yoki

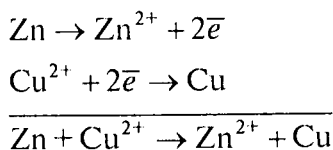


Rux elektrodning normal (standart) potentsiali $\pi_{Zn}^0 = -0,763 \text{ V}$ va mis elektrodning normal potentsiali $\pi_{Cu}^0 = +0,337 \text{ V}$ ga teng. Element sxema tarzida yozilganda chap tomonda elektrmanfiyroq va o'ng tomonda elektrmusbatroq elektrod yoziladi.

Agar bu elektrodlar elektr o'tkazuvchi sim (masalan, mis sim) orqali birlashtirilsa, potentsiallar tenglashishga intiladi va elektronlar manfiy elektrodan elektr musbat elektrodga tomon o'ta boshlaydi (yuqoridagi misolda $Zn \xrightarrow{\bar{e}} Cu$).

Natijada elektronlarning yo'nalgan to'plami — elektr oqimi vujudga keladi. Elektrodagi qo'shqavat muvozanati buziladi, natijada elektrmanfiy elektrod musbatlashadi, elektrmusbat elektrod manfiylashadi. Muvozanatni tiklash uchun manfiy elektrodga ketayotgan elektronlar o'rnini bosadigan yangi elektron quyidagi reaksiya $Zn \rightarrow Zn^{2+} + 2\bar{e}$ natijasida hosil bo'ladi. Elektrmusbat

elektrodda elektronlar quyidagi reaksiya: $\text{Cu}^{2+} + 2\bar{e} \rightarrow \text{Cu}$ natijasida yo'qotiladi. Galvanik element ishlaganda bir tomonda oksidlanish va ikkinchi tomonda qaytarilish reaksiyasi boradi. Shartli ravishda oksidlanish reaksiyasi borayotgan elektrodga manfiy qutb (—) va qaytarilish reaksiyasi borayotgan elektrodga musbat qutb (+) deyiladi. Ya'ni, manfiy qutbda oksidlanish, musbat qutbda qaytarilish reaksiyasi boradi. Galvanik elementda borayotgan umumiy reaksiya oksidlanish-qaytarilish reaksiyasidir:



Shu reaksiya natijasida ajralgan kimyoviy energiya hisobiga elektr energiya E , ya'ni elektr yurituvchi kuch (EYuK) paydo bo'ladi. Agar diffuzion potensial yo'qotilsa,

$$E = \pi_2 - \pi_1. \quad (\text{IX.6})$$

2-elektromusbat elektrodga, 1-elektromanfiy elektrodga tegishlidir:

$$E = E_0 + \frac{RT}{ZF} \ln \frac{a_2}{a_1}. \quad (\text{IX.7})$$

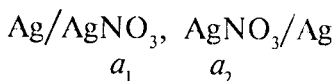
Bunda:

$$E_0 = \pi_2^0 - \pi_1^0,$$

π_2^0, π_1^0 — normal potentsiallar.

Katta aniqlik talab qilinmaydigan hisoblar uchun termodinamik aktivlik (a) o'rniga konsentratsiya ifodasi (c)ni qo'llash mumkin.

Konsentratsion galvanik elementlar. Bu xil galvanik elementlar bir xil elektrolit moddaning turli konsentratsiyadagi eritmasiga tushirilgan bir xil metall (modda) elektrodan iborat bo'ladi. Masalan,



EYuK diffuziyalanish hisobiga hosil bo'ladi:

$$E = \frac{RT}{ZF} \ln \frac{a_2}{a_1}. \quad (\text{IX.8})$$

$E_0 = 0$ bo'ladi.

Galvanik element termodinamikasi. Galvanik elementning EYuKni o'lchash orqali — vodorod ioni konsentratsiyasi (pH), cruvchanlik ko'paytmasi, termodinamik aktivlik kabi kattaliklarni aniqlash mumkin.

Elektrokimyoviy reaksiyalar uchun termodinamik funksiya A , ΔH , ΔS , ΔF , ΔG lar quyidagi tenglamalar yordamida aniqlanadi:

$$\Delta G = -A = -nFE \quad (\text{IX.9})$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p \quad (\text{IX.10})$$

$$\Delta H = -nFE + nT \left(\frac{\partial E}{\partial T} \right)_p \quad (\text{IX.11})$$

$$\Delta C_p = -nFT \cdot \frac{\partial^2 E}{\partial T^2} \quad (\text{IX.12})$$

$$E = -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_p. \quad (\text{IX.13})$$

Izoterma tenglamasi:

$$-\Delta G = RT \left(\ln K - \ln \frac{a_2 a_4}{a_1 \cdot a_3} \right)$$

$\Delta G = -nFE$ qo'yilsa va $a_1 = a_2 = a_3 = a_4 = 1$ qabul qilinsa, unda $E = E_0$ va bu EYuK ni standart EYuK (E_0) deyiladi. Unda $E_0 = \pi_2^0 - \pi_1^0$.

$$\left. \begin{aligned} E_0 &= \frac{RT}{ZF} \ln K \\ \ln K &= \frac{ZFE^0}{RT} = \frac{ZF(\pi_2^0 - \pi_1^0)}{RT} \end{aligned} \right\} \quad (\text{IX.14})$$

MASALALAR YECHISHIGA DOIR MISOLLAR

1. 298 K da $\text{Cu}^{2+}(a = 0,005)\text{Cu}$ elektrod potentsiali 0,2712 V ga teng. Mis elektrodning standart potentsiali π_{Cu}^0 ni aniqlang.

Yechish. (IX. 1) tenglamaga muvofiq:

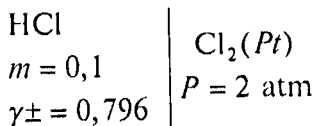
$$\pi = \pi^0 + \frac{RT}{ZF} \ln a_{\text{Cu}^{2+}} = \pi^0 + \frac{0,0591}{2} \ln a_{\text{Cu}^{2+}}$$

Bu tenglamalarda $\ln$ dan $\lg$ ga o'tish va 298 K da

$$\frac{RT \cdot 2,303}{F} = 0,0591 \text{ bo'lishi hisobga olinsa,}$$

$$\pi^0 = \pi - \frac{0,0591}{2} \ln a_{\text{Cu}^{2+}} = 0,2712 - 0,02951 \ln 0,005 = 0,3098 \text{ V.}$$

2. 298 K da xlor elektrodning potentsialini aniqlang.



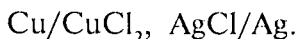
$$\pi_{\text{Cl}}^0 = 1,358 \text{ V ga teng.}$$

Yechish. (IX. 5) tenglamaga muvofiq gaz elektrodning potentsiali:

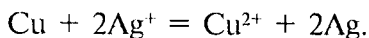
$$\pi = \pi^0 - \frac{0,0591}{1} \lg(a_{\text{Cl}^-} / P^{\frac{1}{2}}) =$$

$$= 1,358 - \frac{0,0591}{1} [\lg(0,1 \cdot 0,796) - \frac{1}{2} \lg 2] = 1,440 \text{ V.}$$

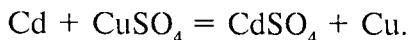
3. Quyidagi galvanik elementning elektrodlarida va galvanik elementda boradigan reaksiya tenglamalarini yozing:



Y e c h i s h . Mis elektrod manfiy qutb bo'lganligidan unda oksidlanish reaksiyasi $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\bar{e}$, kumush elektrod musbat qutb bo'lganligidan unda qaytarilish reaksiyasi $\text{Ag}^+ + \bar{e} \rightarrow \text{Ag}$ boradi. Galvanik elementda quyidagi oksidlanish-qaytarilish reaksiyasi boradi:



4. Quyidagi reaksiya boradigan galvanik element sxemasini tuzing:

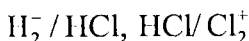


Y e c h i s h . Bu reaksiyada Cd oksidlanayapti: $\text{Cd} \rightarrow \text{Cd}^{2+} + 2\bar{e}$, mis esa qaytarilayapti: $\text{Cu}^{2+} + 2\bar{e} \rightarrow \text{Cu}$. Demak, kadmiy elektrod manfiy va mis elektrod musbat bo'ladi: $\text{Cd/CdSO}_4, \text{CuSO}_4/\text{Cu}$.

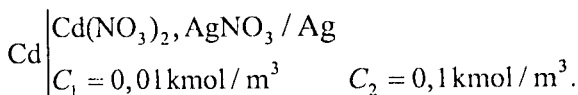
5. $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ reaksiya borayotgan galvanik elementning sxemasini tuzing.

Y e c h i s h . Reaksiyada vodorod oksidlanayapti: $\frac{1}{2} \text{H}_2 = \text{H}^+ + \bar{e}$

va xlor qaytarilayapti: $\frac{1}{2} \text{Cl}_2 + \bar{e} \rightarrow \text{Cl}^-$. Demak:



6. 298 K da quyidagi galvanik elementning EYuK ni aniqlang:



Kumush va kadmiyning standart elektrod potentsiali mos ravishda: $\pi_{\text{Ag}}^0 = 0,799 \text{ V}$, $\pi_{\text{Cd}}^0 = 0,402 \text{ V}$ ga teng.

Y e c h i s h . Avvalo, konsentratsiyani termodinamik aktivlikka $a = \gamma \pm C^+$ o'tkazish kerak. Buning uchun $\gamma_{\pm}$ ni aniqlash kerak. $\gamma_{\pm}$ o'z navbatida ion kuchiga bog'liq. Debay-Xyukkel tenglamasiga muvofiq:

$$\lg \gamma_{\pm} = -A\sqrt{J}.$$

Suvli eritmalar uchun $A = 0,508$ ga teng.

Ma'lum ion kuchiga ega eritmada turli valentli ionlar uchun $\gamma_{\pm}$ ning qiymati ma'lumotnomalarda berilgan.

$$J = \frac{1}{2} \sum C_i Z_i^2$$

$$J_{\text{Cd}(\text{NO}_3)_2} = \frac{0,01 \cdot 1^2 + 0,2 \cdot 1^2}{2} = 0,03 = 3 \cdot 10^{-2}.$$

Ion kuchining bu qiymatida ikki valentli ion uchun $\gamma_{\pm} = 0,053$.

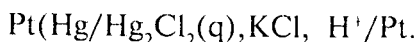
$$J_{\text{AgNO}_3} = \frac{1}{2} \sum C_i Z_i^2 = \frac{0,1 \cdot 1^2 + 0,1 \cdot 1^2}{2} = 0,1.$$

Ion kuchining bu qiymatida ikki valentli ion uchun $\gamma_{\pm} = 0,78$.

$$E = \pi_{\text{Ag}} - \pi_{\text{Cl}} = \left(\pi_{\text{Ag}}^0 + \frac{0,059}{1} \lg a_{\text{Ag}} \right) - \left(\pi_{\text{Cd}}^0 + \frac{0,0591}{2} \lg a_{\text{Cd}} \right) = (0,799 +$$

$$+0,0591 \cdot \lg 0,78 \cdot 0,1) - (0,402 + \frac{0,0591}{2} \lg 0,053 \cdot 0,01) = 1,192 \text{ V.}$$

7. Eritma pH ni aniqlang.



Bu elementning 298 K da EYuK $E = 0,156$ ga teng. Kalomel elektrodning potentsiali $\pi_K = 0,3369 \text{ V}$, xingidron elektrodning standart potentsiali $\pi_{XG}^0 = 0,6994 \text{ V}$ ga teng.

Yechish. Xiron $\text{C}_6\text{H}_4\text{O}_2$ va gidroxiron $\text{C}_6\text{H}_4(\text{OH})_2$ ning ekvimolekular birikmasi $\text{C}_6\text{H}_4\text{O}_2\text{C}_6\text{H}_4(\text{OH})_2$ ga *xingidron (XG)* deyiladi. *XG* ning to'yingan eritmasiga (suvda juda kam miqdorda eriydi) betaraf metall (Pt) tushirilganda hosil bo'ladigan qurilmaga *XG elektrod* deyiladi. *XG* elektrodning potentsiali faqat birgina vodorod ioni konsentratsiyasiga bog'liq:

$$\pi_{XG} = \pi_{XG}^0 + \frac{RT \cdot 2,3}{F} \lg a_{\text{H}^+} = \pi_{XG}^0 + 0,0591 \cdot \lg a_{\text{H}^+}$$

Bunday bog'lanish eritmalarning vodorod ioni konsentratsiyasini *XG* elektrod potentsiali orqali aniqlashga imkon beradi. Buning uchun kalomel elektrod va *XG* elektroddan (*XG* — eritmasida bo'ladi) tashkil topgan galvanik element tuziladi. Bunday galvanik element EYuK:

$$E = \pi_{XG} - \pi_K = \pi_{XG}^0 + 0,0591 \cdot \lg a_{\text{H}^+} - \pi_K,$$

bunda:

$$\text{pH} = \frac{\pi_{XG}^0 - \pi_K - E}{0,059} = \frac{0,6994 - 0,3369 - 0,156}{0,0591} = 3,602.$$

8. Eritmada mis ionining termodinamik aktivligi $a_{\text{Cu}^{2+}}$ ni aniqlang.

Galvanik elementda

$$\text{Cu} \left| \begin{array}{cc} \text{Cu}^{2+}, & \text{Cu}^{2+} \\ a = x & a = 1 \end{array} \right| \text{Cu}$$

298 K da EYuK $E = 0,8885$ V ga teng.

Y e c h i s h . Birorta ma'lum bir ionning termodinamik aktivligi yoki aktivlik koeffitsiyentini aniqlash uchun shu critma va kalomel yoki potentsiali ma'lum bo'lgan boshqa bir elektroddan iborat galvanik element tuziladi va bu elementning EYuK ini o'lchash orqali a yoki $\gamma_{\pm}$ aniqlanadi:

$$E = \pi_2 - \pi_1 = E_0 + \frac{0,0591}{z} \lg \frac{a_2}{a_1} = \frac{0,0591}{z} \lg \frac{1}{x} = -\frac{0,0591}{z} \lg x.$$

Tuzilgan galvanik element konsentratsion element bo'lganligi uchun:

$$\lg x = -\frac{2 \cdot E}{0,0591} = -\frac{2 \cdot 0,8885}{0,0591} = -30,07$$

va

$$a_{\text{Cu}^{2+}} = x = 10^{-31}.$$

9. 298 K haroratda $\text{ZnSO}_4 + \text{Cd} \rightleftharpoons \text{CdSO}_4 + \text{Zn}$ reaksiyaning muvozanat konstanta (K)sini aniqlang.

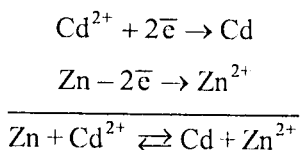
Y e c h i s h . (IX. 14) tenglamaga muvofiq:

$$\lg K = \frac{zE_0}{0,0591} = \frac{z(\pi_+^0 - \pi_-^0)}{0,0591}.$$

Ma'lumotnomalardan rux va kadmiyning standart potentsiallari olinadi:

$$\pi_{\text{Zn}}^0 = -0,762 \text{ V}; \quad \pi_{\text{Cd}}^0 = -0,402 \text{ V}; \quad E^0 = \pi_{\text{Cd}}^0 - \pi_{\text{Zn}}^0.$$

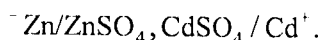
Standart potentsiallarga ko'ra, reaksiya kadmiyning qaytarilish yo'nalishida boradi. Reaksiyada quyidagicha oksidlanish-qaytarilish reaksiyasi boradi:



Demak,

$$K = \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cd}^{2+}}}.$$

K ni elektrokimyoviy usul bilan aniqlash uchun yuqoridagi oksidlanish-qaytarilish reaksiyasi boradigan galvanik elementni tuzish kerak:



Demak,

$$\lg K = \frac{[0,402 - (-0,762)] \cdot 2}{0,0591} = 12,182, \quad K = 1,46 \cdot 10^{12}.$$

10. Kumush xlorid AgCl ning eruvchanlik (L) ko'paytmasini aniqlang.

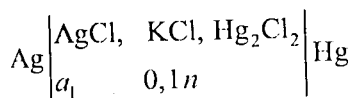
γ_{Cl} — ionning termodinamik aktivlik koeffitsiyenti ma'lumotnomadan olingan: $\gamma_{\text{Cl}^-} = 0,077$; $\pi_{\text{Ag}}^0 = 0,799$.

Y e c h i s h . AgCl ning eruvchanlik ko'paytmasi:

$$L_{\text{AgCl}} = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-}$$

a_{Cl} ma'lum, faqat a_{Ag^+} ni aniqlash kerak. Buning uchun kumush elektrodni potentsiali ma'lum bo'lgan elektrod (odatda, bu xil elektrod sifatida kalomel elektrod olinadi) bilan birlashtirib

galvanik element tuziladi, bu elementning EYuK ini (E) o'lchash kerak:



Elementning EYuKi $E = 0,052$,

$E = \pi_K - \pi_{\text{Ag}}$ va Ag elektrod potentsiali π_{Ag} :

$$\pi_{\text{Ag}} = \pi_K - E = 0,3369 - 0,0525 = 0,2844 \text{ V.}$$

(IX. 1) tenglamaga muvofiq:

$$\pi_{\text{Ag}} = \pi_{\text{Ag}}^0 + 0,059 \lg a_{\text{Ag}^+},$$

bundan:

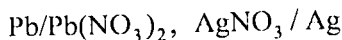
$$\lg a_{\text{Ag}^+} = \frac{\pi_{\text{Ag}} - \pi_{\text{Ag}}^0}{0,0591} = \frac{0,2844 - 0,799}{0,0591} = -8,708, a_{\text{Ag}^+} = 1,96 \cdot 10^{-9}.$$

0,1 n KCl eritmasida:

$$a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} \cdot C = 0,77 \cdot 0,1 = 0,077,$$

$$L_{\text{AgCl}} = 1,96 \cdot 10^{-9} \cdot 0,077 = 1,51 \cdot 10^{-10}.$$

11. Quyidagi



$$a=1 \quad \quad a=1$$

galvanik elementning EYuKini, boradigan reaksiya muvozanat konstantasini va izobarik potensial o'zgarishi ΔG ni aniqlang. Kerakli qiymatlarni ma'lumotnomalardan oling.

Y e c h i s h . (IX.7) tenglama orqali E va E_0 aniqlanadi. So'ngra (IX. 14) tenglamaga ko'ra K va $\Delta G = -RT \ln K$ tenglama yordamida ΔG aniqlanadi.

$E_0 = \pi_{\text{Ag}}^0 - \pi_{\text{Pb}}^0$ elektrodning standart potentsiallari ma'lumotnomalardan olinadi:

$$\pi_{\text{Ag}}^0 = 0,799 \text{ V}; \quad \pi_{\text{Pb}}^0 = 0,126 \text{ V}.$$

Demak,

$$E_0 = \pi_{\text{Ag}}^0 - \pi_{\text{Pb}}^0 = 0,799 - 0,126 = 0,925 \text{ V}.$$

E ni aniqlash:

$$E = E_0 + \frac{0,0591}{z} \lg \frac{a_{\text{Ag}^+}}{a_{\text{Pb}^{2+}}} = 0,925 + \frac{0,0591}{2} \lg \frac{1}{1} = 0,925 \text{ V}.$$

Demak, $E = E_0 = 0,925$.

(IX. 14) tenglama bilan K aniqlanadi:

$$\lg K = \frac{E_0 \cdot 2}{2,303 \cdot 0,0591} = \frac{1,850}{0,1351} = 13,6$$

$$K = 3,95 \cdot 10^{13}$$

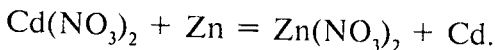
va

$$\Delta G = -2,303 RT \lg K = -2,3 \cdot 8,31 \cdot 10^3 \cdot 298 \cdot 13,6 = -1,78 \cdot 10^7$$

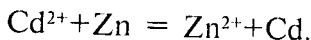
yoki

$$\begin{aligned} \Delta G &= -zFE = 2 \cdot 9,5 \cdot 10^7 \cdot 0,925 = \\ &= -1,78 \cdot 10^7 \text{ J/kmol} = 24,4 \text{ kkal/mol.} \end{aligned}$$

12. Galvanik elementda quyidagi reaksiya boradi:



Ion reaksiyasi:



Ma'lumotnomalarda ionlar uchun keltirilgan termodinamik kattaliklarning standart qiymatlaridan foydalanib reaksiyaning muvozanat konstantasini aniqlang.

Yechish. Muvozanat konstantasini aniqlashda $\Delta G^0 = -2,3RT \lg K$ dan foydalaniladi. Bunda:

$$\lg K = -\frac{\Delta G^0}{2,3RT}$$

tengligidan $\Delta G^0 = \Delta G_{\text{Zn}^{2+}}^0 - G_{\text{Cd}^{2+}}^0$. Ma'lumotnomadan $\text{Zn}^{2+}, \text{Cd}^{2+}$ ionlarining standart izobarik potentsiallarini topamiz:

$$\Delta G_{\text{Zn}^{2+}}^0 = -147,30 \text{ kJ/mol},$$

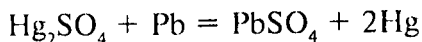
$$\Delta G_{\text{Cd}^{2+}}^0 = -77,794 \text{ kJ/mol},$$

$$\Delta G^0 = -147,30 - (-77,794) = -69,504 \text{ kJ/mol}.$$

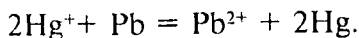
$$\lg K = -\frac{\Delta G^0}{2,3RT} = \frac{69,504}{2,3 \cdot 8,314 \cdot 298} = 12,17;$$

$$K = 1,47 \cdot 10^{12}.$$

13. Galvanik elementda quyidagi reaksiya boradi:



yoki



298 K da entropiyaning o'zgarishi ΔS^0 , EYuKning harorat bilan o'zgarish koeffitsiyenti $\left(\frac{\partial E}{\partial T}\right)$, reaksiyaning standart issiqlik effekti ΔI^0 va EYuK ni aniqlang. Kerakli ma'lumotlarni ma'lumotnomalardan oling.

Yechish. (IX.9—IX. 14) tenglamalardan foydalangan holda ma'lumotnomalardan reaksiyada ishtirok etgan moddalar uchun

entropiyaning mutlaq qiymati ΔS^0 va hosil bo'lgan issiqlik effekti ΔH_{298}^0 olinadi.

Modda	Hg	PbSO ₄	Hg ₂ SO ₄	Pb
$\Delta S_{298}^0, \text{J/mol} \cdot \text{grad}$	76,1	148,67	-100,83	64,85
$\Delta H_{298}^0, \text{kJ/mol}$	0	-918,1	-742,0	0

Entropiya o'zgarishi:

$$\begin{aligned}\Delta S^0 &= (2S_{\text{Hg}}^0 + S_{\text{PbSO}_4}^0) - (S_{\text{Hg}_2\text{SO}_4}^0 + S_{\text{Pb}}^0) = \\ &= (79,1 + 148,62) - (-100,83 + 68,25) = 35,19 \text{ J/mol} \cdot \text{grad}.\end{aligned}$$

EYuKning harorat koeffitsiyenti $\left(\frac{\partial E}{\partial T}\right)_p$.

(IX. 10) tenglamaga ko'ra:

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{zF} = \frac{35,19}{2 \cdot 96486} = 1,8510^{-1} \frac{\text{volt}}{\text{grad}}.$$

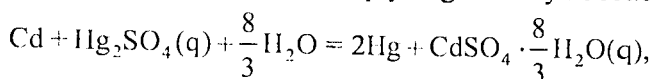
Elementdagi kimyoviy reaksiya issiqlik effekti:

$$\begin{aligned}\Delta H_{298}^0 &= \Delta H_{298, \text{PbSO}_4}^0 - \Delta H_{298, \text{Hg}_2\text{SO}_4}^0 = -918,1 - (0 - 742,0) = \\ &= -176,11 \text{ kJ/mol} = 176,1 \cdot 10^3 \text{ J/mol}.\end{aligned}$$

(IX. 13) tenglamadan EYuK aniqlanadi:

$$E = -\frac{\Delta H^0}{zF} + T \left(\frac{\partial E}{\partial T}\right) = \frac{-176,1 \cdot 10^3}{2 \cdot 96487} + 298 \cdot 1,85 \cdot 10^{-1} = 0,9686 \text{ V}.$$

14. Veston galvanik elementida quyidagi reaksiya boradi:



uning EYuK harorat bilan quyidagicha o'zgaradi:

$$E = 1,018 - 0,041 \cdot 10^{-3}(t - 20) - 9,5 \cdot 10^{-7}(t - 20)^2 + 10^{-8} - 20)^3.$$

298 K da ΔC_p ni aniqlang.

Yechish. (IX. 12) tenglamaga muvofiq: $\Delta C_p = zFT \left(\frac{\partial^2 E}{\partial T^2} \right).$

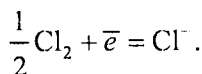
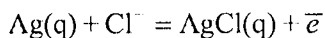
Demak, $E = f(T)$ tenglamani ikki marta differensiallash kerak:

$$\left(\frac{\partial^2 E}{\partial T^2} \right) = -16 \cdot 10^{-7} \frac{\text{volt}}{\text{grad}}$$

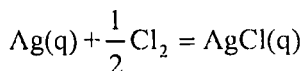
va (IX. 12) tenglamaga muvofiq:

$$\Delta C_p = zFT \left(\frac{\partial^2 E}{\partial T^2} \right) = -2 \cdot 96478 \cdot 298 \cdot 16 \cdot 10^{-7} = 92,1 \text{ J/mol} \cdot \text{grad}.$$

15. $\text{Ag}/\text{AgCl}(\text{q}), \text{HCl}_1 \cdot n\text{H}_2\text{O}/\text{Cl}_2(\text{Pt})$ galvanik elementda quyidagi reaksiya boradi:



Agar bu reaksiyalar jamlansa:



kumush va xlordan AgCl kristali hosil bo'lish reaksiyasining issiqlik effektini hisoblang:

$$\left(\frac{\partial E}{\partial T} \right)_p = 0,000477 \frac{\text{volt}}{\text{grad}}; \quad E = 1,132 \text{ V}.$$

Yechish. $\Delta G = \Delta H - T\Delta S$, $\Delta H = \Delta G + T\Delta S$. Shunga ko'ra, (IX.7) tenglamadan ΔG va (IX. 10) tenglama bilan ΔS aniqlanadi.

$$\Delta G = -zFE = -1 \cdot 23062 \cdot 1,132 = -26106 \text{ kal.}$$

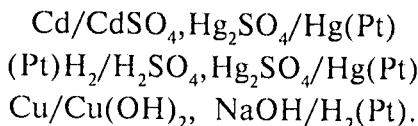
$$\Delta S = zF \left(\frac{\partial E}{\partial T} \right) = 1 \cdot 23062 \cdot 0,000477 = 11,0 \text{ kal/grad.}$$

$$T\Delta S = 298 \cdot 11,0 = 3280 \text{ kal.}$$

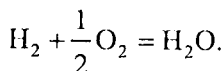
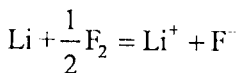
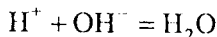
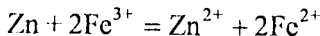
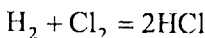
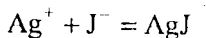
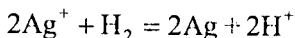
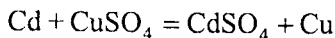
$$\Delta H = \Delta G + T\Delta S = -26106 + 3280 = -22826 \text{ kal.}$$

MASALALAR

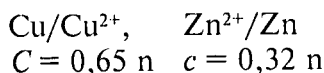
1. Masalalarni yechish uchun kerakli ma'lumotlarni ilova (ma'lumotnoma)dan oling. Quyidagi galvanik elementlarning manfiy va musbat qutblarida va umuman, elementda boradigan reaksiyalar tenglamalarini yozing.



2. Quyidagi reaksiyalar boradigan elektrodlar va galvanik elementlarning sxemalarini yozing.



3. Quyidagi elementning



EYuKini aniqlang. Tuzlarning normal critmalari dissotsilanish koeffitsiyenti $\alpha = 0,23$ ga teng.

4. Quyidagi elementning

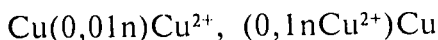


18°C dagi EYuK $E = 1,098$ V. Rux ionining konsentratsiyasi 0,4 g ga, misniki 1 litrda 2 g ionga teng bo'lganida EYuK qanchaga teng bo'ladi?

5. Cu^{2+}/Cu chegarasida potensial $\pi = +0,344$ V. Bu chegarada potensial nolga teng bo'lishi uchun mis ioni konsentratsiyasini qanchaga kamaytirish kerak?

6. $\text{Zn}(0,01 \text{ n})/\text{Zn}^{2+}$, 1 n $\text{KClHg}_2\text{Cl}_2/\text{Hg}(\text{Pt})$ galvanik elementning 25°C dagi EYuK i $E = 1,0996$. Ruxning normal potensialini aniqlang. Kalomel elektrodning potentsiali nolga teng deb qabul qilinsin.

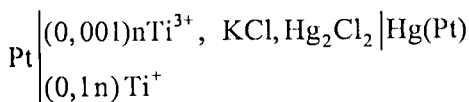
7. Quyidagi konsentratsion galvanik elementning



EYuKini aniqlang.

8. 25°C da quyidagi elektrodning $\text{Cu}/\text{Cu}^{2+}(\alpha = 0,005)$ potentsiali $\pi = 0,2712$ V. Bu elektrodning standart potentsiali π^0 ni aniqlang.

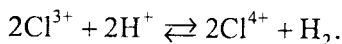
9. Quyidagi elementning



EYuKini aniqlang. $\pi_{\text{oks-qayt}}^0 = 0,056$. Kalomel elektrod potentsiali nolga teng deb qabul qilinsin.

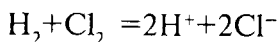
10. $\text{Pt} \left| \begin{array}{l} 90\% \text{Cl}^{4+} \\ 1\% \text{Cl}^{3+} \end{array} \right. , \text{KCl}, \text{Hg}_2\text{Cl}_2 / \text{Hg}(\text{Pt})$. Galvanik elementning

EYuK i $E = 1,464 \text{ V}$. Quyidagi reaksiyaning muvozanat konstantasini aniqlang. $\pi_{\text{oks-qayt}}^0 = 1,567 \text{ V}$.



11. $\text{Cl}^{2+} + \text{Zn} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$ reaksiyaning muvozanat konstantasini aniqlang. $\pi_{\text{Cu}}^0 = +0,153$, $\pi_{\text{Zn}}^0 = -0,763 \text{ V}$.

12. Xlor elektrodning standart potensialidan foydalanib,



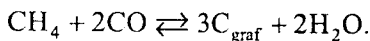
reaksiyaning muvozanat konstantasini aniqlang.

13. 25⁰da Zn^{2+}/Zn chegarasida elektrod potensial $\pi_{\text{Zn}} = -0,758 \text{ V}$, Cd^{2+}/Cd chegarasida esa $\pi_{\text{Cd}} = -0,395 \text{ V}$.

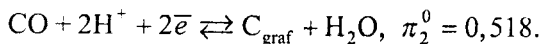
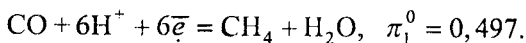
$\text{Zn} + \text{Cd}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cd}$ reaksiyaning muvozanat konstantasini

(K) aniqlang.

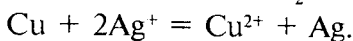
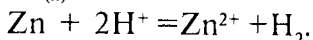
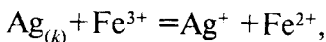
14. Quyidagi reaksiyaning muvozanat konstantasini aniqlang.



25⁰C da:

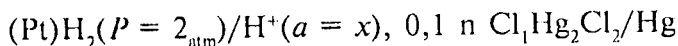


15. Quyidagi reaksiyalarning muvozanat konstantalarini aniqlang.



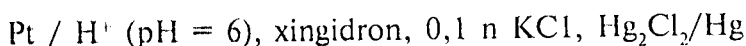
Elektrodlarning standart potensialini ilova (ma'lumotnoma)dan oling.

16. Quyidagi galvanik elementning



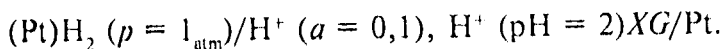
EYuK i $25^\circ C$ da $E = 0,5 \text{ V}$ ga teng. pH ini aniqlang, $\pi_K^0 = 0,3369 \text{ V}$.

17. Quyidagi galvanik elementning



$25^\circ C$ da EYuKini aniqlang. Xingidron elektrodining standart potentsiali $\pi_{XG}^0 = -0,6994 \text{ V}$.

18. Quyidagi galvanik elementning EYuKini aniqlang:

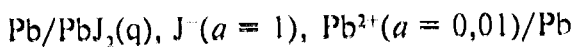


Standart xingidron elektrod potentsiali $\pi_{XG}^0 = 0,6994 \text{ V}$.

19. Kumush elektrod Ag^+/Ag va xlor-kumush elektrod $Cl^-/AgCl$, Ag larning standart elektrod potentsialidan foydalanib, $25^\circ C$ da $AgCl$ ning eruvchanlik ko'paytmasini aniqlang.

20. Elektrodlarning normal elektrod potentsialidan foydalanib, 298 K da kumush galoidlarning eruvchanliklari nisbatini $L_{AgCl}: L_{AgBr}: L_{AgI}$ aniqlang.

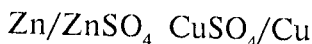
21. $25^\circ C$ da quyidagi galvanik elementning



EYuK i $E = 0,1728 \text{ V}$ ga teng. PbJ_2 ning eruvchanligini aniqlang.

22. $Cd/CdJ_2, AgJ(q)/Ag$ galvanik elementning EYuK $25^\circ C$ da $E = 0,2860 \text{ V}$ ga teng. Eritmadagi CdJ_2 ning termodinamik aktivligini aniqlang.

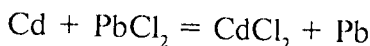
23. $\text{Pb}/\text{PbSO}_4(\text{q}), \text{CuSO}_4(m = 0,02)/\text{Cu}$ elementning 25°C da EYuK i $E = 0,5594 \text{ V}$. CuSO_4 ning o'rtacha termodinamik aktivligini aniqlang.
24. Quyidagi galvanik elementning



0°C da EYuK $E_1 = 1,0962 \text{ V}$, 30°C da esa $E_2 = 1,0963 \text{ V}$.

Bu galvanik elementda borayotgan reaksiyaning issiqlik effekti qanchaga teng?

25. Quyidagi reaksiya



boradigan galvanik elementning EYuK i 25°C da $E = 0,1880 \text{ V}$ ga

teng. $\left(\frac{\partial E}{\partial T}\right)_p = -4,8 \cdot 10^{-4} \text{ V/grad}$. Reaksiyaning issiqlik effekti va

entropiya o'zgarishini aniqlang.

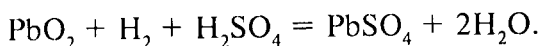
26. Yuqori haroratda ishlaydigan galvanik elementlarga xos ma'lumotlar quyida keltirilgan. Metallarni xlrlash reaksiyasi uchun ΔG , ΔH , ΔS ni aniqlang.

Galvanik elementda boradigan reaksiya	EYuK, V	Harorat, K
$\text{Mg}_{(\text{C})} + \text{Cl}_{(2)} = \text{MgCl}_{2(\text{C})}$	$E = 3,068 - 5,70 \cdot 10^{-4} T$	1200
$\text{Cd} + \text{Cl}_2 = \text{CdCl}_2$	$E = 2,266 - 3,5 \cdot 10^{-4} T$	600

27. $\text{Ag} + \frac{1}{2} \text{Hg}_2\text{Cl}_2 = \text{AgCl} + \text{Hg}$ reaksiya boradigan galvanik

elementning EYuK i 25°C da $E_1 = 0,0455 \text{ V}$, 20°C da esa $E_2 = 0,0422 \text{ V}$ ga teng. 25°C da ΔG , ΔH va ΔS ni aniqlang.

28. Galvanik elementda quyidagi reaksiya boradi:



Reaksiyada ishtirok qilayotgan har bir moddaning aktivligi $\alpha = 1$ ga teng. Vodorodning bosimi $p = 1,93 \cdot 10^5$ Pa ga teng. Galvanik elementning EYuK i harorat bilan quyidagicha o'zgaradi:

Harorat, K	EYuK, V
293	1,68322
298	1,68488
303	1,68671

ΔG , ΔH va ΔS ni aniqlang.

29. $\text{H}_2 + 2\text{AgBr} = 2\text{Ag} + 2\text{HBr}$ reaksiya boradigan galvanik elementning EYuK i harorat bilan quyidagicha bog'langan:

$$E = 0,07131 - 4,99 \cdot 10^{-4} (t - 25) - 3,45 \cdot 10^{-6} (t - 25)^2.$$

Reaksiyaning issiqlik effektini aniqlang.

KO'P VARIANTLI MASALALAR

1. m_1 va m_2 (1 mol/1000 g) konsentratsiyali B eritmaga A elektrod tushirib konsentratsion galvanik element tuzilgan, 298 K da elementning EYuK ini aniqlang. Termodinamik aktivlik koeffitsiyentining qiymatini ilova (ma'lumotnoma)dan oling yoki suyultirilgan eritmalar uchun ion kuchi qoidasidan foydalanib toping.

№	Modda		m_1	m_2	Modda	m_3	m_4	P_{H_2} , atm
	A	B						
1	Cu	CuCl ₂	1	2	HCl	0,01	0,1	0,20
2	Cu	CuCl ₂	0,2	0,05	HCl	3	0,5	2,00
3	Cu	CuCl ₂	2	0,006	NaOH	2	1	2,00
4	Cu	CuCl ₂	0,02	0,6	NaOH	8	1,5	2,00
5	Cu	CuSO ₄	0,1	0,5	HBr	0,95	4	0,20
6	Cu	CuSO ₄	0,01	1	HBr	1	0,45	0,20
7	Cd	Cd(NO ₃) ₂	0,2	0,61	NaOH	1,4	2	3,00
8	Cu	Cd(NO ₃) ₂	2	0,7	NaOH	0,1	2,5	3,00
9	Cd	CdSO ₄	0,05	2	H ₂ SO ₄	0,5	3	3,00
10	Cd	CdSO ₄	1	0,2	H ₂ SO ₄	17	3,5	0,10

2. m_3 (mol/1000 g) konsentratsiyali c eritmadagi vodorod elektrod va KCl niki m_4 bo'lgan kalomel elektroddan tashkil topgan galvanik elementning EYuK ini va eritma pH ini aniqlang. 298 K da kalomel elektrodning standart potentsiali 0,268 V ga teng.

2-jadvalda keltirilgan reaksiya boradigan galvanik elementlarning EYuK ining haroratga bog'lanish tenglamasi berilgan. Bu reaksiya uchun reaksiya issiqlik effekti ΔH , entropiya ΔS , Gibbs funksiyasi ΔG o'zgarishini hisoblang.

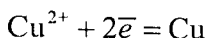
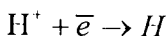
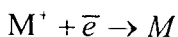
Vari- ant	T, K	Vari- ant	T, K	Reaksiya	E = f(m)
1	273	2	323	$C_6H_4O_2 + 2H^+ =$ $C_6H_4(OH)_2 + 2e^-$	$E = 0.6990 - 7,4 \cdot$ $\cdot 10^{-4} (T - 298)$
3	343	4	363	$Zn + 2AgCl = ZnCl_2 + 2Ag$	$E = 1.125 - 4,02 \cdot 10^{-4}$
5	278	6	313	$Zn + H_2SO_4 =$ $ZnSO_4 + 2H_2$	$E = 1.8328 - 1.19 \cdot$ $\cdot 10^{-3} (T - 298)$
7	273	8	298	$Ag^+ + Cl^- = AgCl + e^-$	$E = 0.2224 - 6,4 \cdot 10^{-4} (T - 298)$
9	273	10	363	$Cd + H_2SO_4 =$ $CdSO_4 + 2H_2$	$E = 1.0183 - 4,06 \cdot$ $\cdot 10^{-3} (T - 298)$
11	303	12	273	$Cd + 2AgCl = CdCl_2 + 2Ag$	$E = 0,869 - 0,5 \cdot 10^{-4} T$
13	293	14	323	$Cd + PbCl_2 = CdCl_2 + Pb$	$E = 0.331 - 4,8 \cdot 10^{-4} T$
15	273	16	363	$2Hg + ZnCl_2 =$ $Hg_2Cl_2 + Zn$	$E = 1 + 9,4 \cdot 10^{-5} (T - 298)$
17	273	18	353	$2Hg + SO_4^{2-} =$ $Hg_2SO_4 + 2e^-$	$E = 0.0.6151 - 8,02 T$
19	333	20	353	$Pb + 2AgJ = PbJ_2 + 2Ag$	$E = 0,259 - 1,3,8 \cdot 10^{-4} T$
21	273	22	398	$2Hg + 2Cl^- = Hg_2Cl_2 + 2e^-$	$E = 0,22438 - 6,5 \cdot$ $\cdot 10^{-4} (T - 298)$

X bob

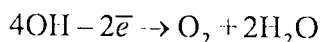
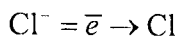
ELEKTROKIMYOVIY REAKSIYALAR KINETIKASI. ELEKTROLIZ

Elektrolit eritmalar yoki suyuqlanmalardan turg'un elektr oqimi o'tkazilganda, qutblarda galvanik element elektrodlarida reaksiyalar teskari boradi. Musbat va manfiy qutblarda qaytarilish reaksiyalari boradi. Bu reaksiyalar natijasida qutblarda moddalar ajralib chiqadi. Kationlar manfiy qutb, anionlar musbat qutb tomon boradi. Shunga ko'ra, manfiy qutb ***katod*** va musbat qutb ***anod*** deb ataladi.

Katodda



Anodda



Elektrodda ajralib chiqayotgan moddalarning miqdori Faradeyning ikki qonunida ifodalangan.

Birinchi qonun: elektrodda ajralib chiqayotgan modda miqdori faqat elektr oqim miqdori — kulonlar ($Q = It$) soniga bog'liq.

Ikkinchi qonun: elektrodda moddalar ekvivalent massa miqdorlariga mutanosib ravishda ajralib chiqadi. Bir g-atom ekvivalent modda ajralib chiqishi uchun 1 Faradey amper-sekund, ya'ni 96487(96500) kulon kerak bo'ladi. Bu son *Faradey soni*

(F) deb ataladi. $F = 96500$ kulon = 23062 kal = $\frac{96500}{60 \cdot 60} = 26,8$

amper-soat bo'ladi. Demak, elektrolizga uchragan modda miqdori:

$$E = \frac{Q}{F} = \frac{It}{F},$$

bunda: E — ekvivalent massa; I — oqim kuchi; t — vaqt (sekund); F — Faradey soni.

Eritmadan 1 kulon elektr oqimi o'tganda ajralib chiqqan modda miqdoriga *elektrokimyoviy ekvivalent* deyiladi. AgNO_3 eritmasidan 1 kulon elektr oqimi o'tganda katodda 1,118 g kumush ajralib chiqadi. Demak, kumushning elektrokimyoviy ekvivalenti 1,118 g ga teng. $E_e = E_k / 26,8$.

Eritmadan Q (amper-soat) elektr miqdori o'tganda elektrodda ajralib chiqadigan moddaning massasi $m = \frac{I \cdot L \cdot E_k \cdot Z}{26,8} = I \cdot t \cdot E_e \cdot Z$.

Amalda berilgan elektr oqimining bir qismi yonaki reaksiyalarga sarf bo'ladi va natijada elektrolizda elektrodlarda Faradey qonuniga muvofiq chiqishi kerak bo'lgan miqdordan kam modda ajralib chiqadi. Shunga ko'ra, odatda, oqim bo'yicha unum hisoblanadi:

$$A = \frac{a}{b},$$

bunda: a — amalda chiqqan modda miqdori; b — Faradey qonuniga muvofiq ajralib chiqishi kerak bo'lgan modda miqdori.

MASALALAR YECHISHGA DOIR MISOLLAR

1. CuSO_4 eritmasidan 5 amper-soat elektr oqimi o'tkazilgan va bunda katod elektrodda 5,6 g mis ajralib chiqqan. Oqim bo'yicha unumni aniqlang.

Y e c h i s h . Amper-soatni kulonga aylantirish kerak:

$$\left. \begin{array}{l} 1F - 26,8 \text{ ac} \\ x - 5 \end{array} \right\} x = \frac{5}{26,8} = 0,1866 F.$$

Demak, elektrodlardan shuncha miqdor zaryad oqib o'tganida qancha gramm mis ajralib chiqishi kerak? $M_{sm} = 63,546$; valentlik 2 ga teng. Demak, g-ekvivalent: $63,76/2 = 31,773$.

$$\left. \begin{array}{l} 1F 31,785 \text{ g mis} \\ 0,1866 - x \text{ g mis} \end{array} \right\} x = 31,773 \cdot 0,1866 = 5,93.$$

Shu sababli oqim bo'yicha unum:

$$A = \frac{5,6}{5,93} \cdot 100 = 94,4\%.$$

2. Sulfat kislota eritmasidan 5 minut davomida elektr toki o'tkazilganda katodda 298 K va 748 mm sim. ust. bosimida 40 sm³ vodorod ajralib chiqqan. O'tkazilgan elektr toki kuchini (J) aniqlang.

Yechish. Ajralgan vodorodning massasini topish kerak. $pV = nRT$ tenglamadan foydalanib topiladi:

$$n = \frac{g}{M}; \quad g = \frac{MpV}{RT}$$

$$M_{H_2} = 2,016; \quad P = 748/760 \text{ atm.}$$

$$V = 0,04 \text{ l, } R = 0,082 \text{ l-atm./grad} \cdot \text{mol.}$$

Bu qiymatlar yuqoridagi tenglamaga qo'yilsa:

$$g = \frac{2,016 \cdot 748 \cdot 0,04}{760 \cdot 0,082 \cdot 298} = 0,0032 \text{ g H}_2$$

$$Q = It \text{ va } J = \frac{Q}{t}.$$

Demak, I ni aniqlash uchun eritmadan qancha kulon (Q) o'tganligini bilish kerak. Ma'lumki, 1 Faradey (96500 kulon)

elektr o'tganda 1 g-ekvivalent $E = \frac{M}{z} = 1,008 \text{ g}$ vodorod ajralib

chiqadi. Boshqacha aytganda, 1,008 g vodorod ajralib chiqishi uchun 1 Faradey elektr toki (96500 kulon) talab qilinadi. 0,0032 g vodorod ajralib chiqishi uchun qancha kulon kerak bo'ladi?

Ya'ni:

$$Q = \frac{0,0032 \cdot 96500}{1,008}.$$

Demak:

$$I = \frac{Q}{t} = \frac{0,0032 \cdot 96500}{1,008 \cdot 300} = 1,02 \text{ A.}$$

3. Yuzasi $10 \times 10 \text{ sm}^2$ bo'lgan plastinkaning ikki tomonini 0,05 mm qalinlikdagi nikel qatlami bilan qoplash kerak. Buning uchun $\text{Ni}(\text{NO}_3)_2$ eritmasidan kuchi 2 amper bo'lgan elektr toki o'tkazilgan. Qoplash uchun kerakli nikelni olish uchun elektr tokini qancha vaqt davomida yuborish kerak bo'ladi? Nikelning zichligi $d = 8,9 \text{ g/sm}^3$. Oqim bo'yicha unum 96% ga teng.

Yechish. Qoplash kerak bo'lgan yuza 200 sm^3 ga teng. Demak, qoplanishi kerak bo'lgan hajm $200 \cdot 0,005 = 1,0 \text{ sm}^3$.

Bu hajmdan nikelning massasi aniqlanadi:

$$d = \frac{g}{v}; \quad g = dv = 8,9 \text{ g.}$$

Nikelning atom massasi $A = 58,69$ va valentligi 2 ga teng. Demak, uning 1 g-ekvivalenti $E = 29,35$ ga teng. 8,9 g ga esa 0,303 g-ekvivalent to'g'ri keladi. Bu miqdorda nikel ajralib chiqishi uchun (nazariy) $0,303 \cdot 26,8 = 8,12$ amper-soat tok kerak bo'ladi. Agar oqim bo'yicha A (unum) e'tiborga olinsa, $8,12/0,96 = 8,46$ amper-soat kerak bo'ladi.

Demak,

$$Q = It; \quad t = \frac{Q}{I} = \frac{8,46}{2} = 4,13,$$

ya'ni 4 soat 13 minut.

MASALALAR

1. Sulfat kislotaning suyultirilgan eritmasidan elektr oqimi 10 minut davomida yuborilganda ajralgan vodorodning 17°C va 760 mm sim. ust. bosimidagi hajmi 100 sm^3 ga teng bo'lgan. O'rtacha elektr toki kuchini aniqlang.

2. Mis xlorid eritmasidan 30 minut davomida 2,3 amper elektr oqimi yuborilgan. Elektroliz davomida qancha CuCl_2 ajralgan?

3. Mis bromidning suvdagi eritmasida 45 minut davomida 20 g mis bromid ajralishi uchun elektr oqimi kuchi qancha bo'lishi kerak?

4. Mis sulfat, qo'rg'oshin nitrat, kumush nitrat va vismut nitrat eritmalaridan 1 amper-soat elektr oqimi yuborilgan. Har qaysi metallning qancha gramm-ekvivalenti ajralib chiqadi?

5. Nikel sulfat eritmasidan 1 amper-soat elektr oqimi o'tganda katodda nikel va vodorod ajralib chiqqan. Ajralib chiqqan nikel qiymati 0,342 g-ekv. ga teng. Erkin holda necha g-ekv. vodorod ajralib chiqqan?

6. CuCl_2 eritmasidan 2 amper elektr toki 2 soat davomida o'tkazilganda katodda qancha gramm mis ajralib chiqdi? Agar shu sharoitda CuCl_2 ni Cu_2Cl_2 bilan almashtirilsa, qayerda qancha mis ajralib chiqadi?

7. 80 sm^3 0,1 molar eritmadagi Fe^{3+} ni Fe^{2+} gacha qaytarish uchun 1 amper elektr oqimini qancha vaqt davomida yuborish kerak bo'ladi?

8. Oqim bo'yicha unum 90% bo'lganda 1 tonna mis olish uchun qancha elektr energiya (Joul) kerak bo'ladi?

9. AgNO_3 , CuSO_4 , KJ, HClO_4 har qaysi eritmadan elektr oqimi o'tkazilganda platina elektrodda AgNO_3 eritmasida 0,1079 g kumush ajralib chiqqan. CuSO_4 , KJ, HClO_4 eritmalarida qanday modda va qancha miqdorda ajraladi?

10. KJ eritmasidan 1 soat davomida turg'un elektr oqimi yuborilgan. Ajralgan yodni titrlash uchun 200 sm^3 0,05 molar $\text{Na}_2\text{S}_2\text{O}_3$ eritmasi sarflangan. Elektr oqimi kuchini aniqlang.

11. Nikel sulfat NiSO_4 eritmasidan elektr oqimi yuborilganda katodda nikel va vodorod birga ajralgan. Eritmadan 0,5 amper-soat elektr o'tkazilganda (n.sh.da) $7,4 \text{ sm}^3$ vodorod ajralib chiqqan. Nikelda ajralib chiqish oqimi bo'yicha unumini aniqlang.

12. Rux sulfat ZnSO_4 eritmasidan elektr oqimi o'tkazilganda katodda rux bilan birgalikda vodorod ham ajralib chiqqan. Eritmadan 20 amper-soat elektr oqimi yuborilganda va ruxning oqim bo'yicha unumi 90% bo'lsa, katodda necha gramm rux va qancha hajm vodorod (n. sh. da) ajralib chiqadi?

13. Natriy sulfat Na_2SO_4 eritmasidan 4 A kuchga ega elektr oqim 10 soat davomida o'tkazilgan. Katod va anod maydonlari bir-biridan ajratilgan. Katodda NaOH va anodda H_2SO_4 hosil bo'ladi. Ishqor va kislotaning konsentratsiyasini aniqlang. Katod uchastkasi hajmi 5 l, anod maydoni hajmi 8 l ga teng.

14. Yuzasi 100 sm^2 bo'lgan metall qurilma 0,3 mm qalinlikda elektr vositasida nikel qatlami bilan qoplanishi kerak. 3 amper kuch bilan elektr oqimi eritmada o'tkazilganda cho'ktirish qancha vaqt davom etishi kerak? Agar nikelning oqim bo'yicha unumi 90% bo'lsa, qoplashga qancha vaqt kerak bo'ladi? Nikelning zichligi 9 g/sm^3 .

15. Rux tuzi elektroliz qilinganda umumiy yuzasi 100 sm^2 bo'lgan tunukadan katod sifatida foydalanilgan. Eritmadan 25 minut davomida 2,5 amper kuchli elektr oqimi o'tkazilgan. Ruxning zichligi $7,15 \text{ g/sm}^3$ ga teng. Tunukani qoplagan rux qatlamining qalinligi qancha?

16. 15% li 2 l NaOH eritmasidan 5 amper elektr oqimi 3 sutka davomida yuborilgan. Elektrolizdan so'ng NaOH ning konsentratsiyasini aniqlang. 15% li NaOH eritmasining zichligi $1,1665 \text{ g/sm}^3$ ga teng.

XI bob

KIMYOVIY REAKSIYALAR KINETIKASI

XI.1. RASMIY KINETIKA

Kimyoviy kinetika reaksiyalarning tezligi, bu tezlikka turli omillarning (konsentratsiya, harorat, katalizator va hokazolar) ta'siri va reaksiyaning mexanizmi (borish yo'llari)ni o'rganadigan fandır. Rasmiy kinetika reaksiya tezligiga reaksiyaga kirishuvchi moddalar konsentratsiyalarining ta'sirini o'rganadi. Reaksiyaning tezligi vaqt birligida moddalar konsentratsiyasining o'zgarishiga tengdir. Reaksiya davomida sistemadagi reaksiyaga kirishayotgan moddalar va hosil bo'lgan mahsulotlar ekvivalent miqdorda o'zgaradi. Shunga ko'ra, reaksiyalarning tezligini vaqt o'tishi bilan dastlabki moddalarning birontasining kamayishi yoki mahsulotdan birontasining ko'payishini kuzatish (o'lchash) bilan aniqlash mumkin. Biz faqat gomogen sistema reaksiyalarining, ya'ni reaksiyada ishtirok qiluvchi hamma moddalar bir fazada (faqat suyuqlik yoki faqat gazlar) bo'ladigan sistemadagi reaksiyalar to'g'risida bahs yuritamiz.

Reaksiya tezligiga o'zgarmas haroratda ($T = \text{const}$) konsentratsiyaning ta'sirini massalar ta'siri qonuni ifoda etadi:

$$V = kC_1^{n_1}C_2^{n_2}, \quad (\text{XI.1})$$

bunda: V — kuzatilgan tezlik, ya'ni dastlabki moddalarning ma'lum konsentratsiyada boradigan reaksiya tezligi; C_1 , C_2 — birinchi, ikkinchi va hokazo moddalarning konsentratsiyalari; n_1, n_2 — birinchi va ikkinchi modda konsentratsiyalarining kuzatilgan tezlikka qaysi darajada ta'sir qilishini ko'rsatadi; k — tezlik konstantasi (solishtirma

tezlik) — reaksiyaga kirishuvchi moddalarning konsentratsiyalari bir birlikka teng bo'lgandagi tezlik.

(XI.1) tenglama yordamida k aniqlansa, kuzatilgan tezlikni topish mumkin. Shunga ko'ra, kimyoviy reaksiyalar kinetikasining qonunlari va kinetik tenglamalar k ni hisoblashga qaratilgan.

XI.2. KINETIK SINFLANISH

Reaksiyalar ikki xil belgisi bilan: reaksiya borishiga olib keladigan to'qnashishlardagi to'qnashgan moddalar xilining soni bilan **molekularligi**, ya'ni bir, ikki va hokazo molekular reaksiyalar va **tartibi** bilan reaksiya tezligiga, reaksiyaga kirishayotgan moddalar konsentratsiyalari qanday darajada ta'sir qilishi bilan, ya'ni bir (mono), ikki, uch va hokazo tartibli reaksiyalarga bo'linadi. Bir xil molekular va tartibli reaksiyalarning kinetik qonuniyatlari va tenglamalari bir xil ko'rinishda bo'ladi.

Agar bir vaqtda faqat bitta reaksiya borsa, bunday reaksiyaga **oddiy reaksiya** deyiladi. Agar bir vaqtda bir qancha reaksiya borsa — **murakkab reaksiya** deyiladi.

Reaksiya davomida reaksiyaga kirishuvchi moddalarning miqdori (konsentratsiyasi) uzluksiz o'zgarishi sababli, reaksiya tezligi ham uzluksiz o'zgarganligidan kuzatilgan tezlik (v) ifodasi differensial ko'rinishda beriladi:

$$v = \pm \frac{dC}{dt} = kC_1^{n_1}C_2^{n_2}, \quad (\text{XI.2})$$

bunda: C — konsentratsiya; t — vaqt.

Minus (−) ishorasi reaksiyaga kirishuvchi moddalarning vaqt bo'yicha konsentratsiyasining kamayishini o'lchash (kuzatishi) orqali aniqlansa, plus (+) ishorasi aksincha mahsulotlar konsentratsiyasining o'zgarishini kuzatish orqali aniqlanganda qo'yiladi.

XI.3. REAKSIYA TEZLIGIGA MODDALAR KONSENTRATSIYASINING TA'SIRI

A. Oddiy reaksiyalar

Birinchi tartibli (va monomolekular) reaksiyalar uchun:

$$-\frac{dC}{dt} = kC, \quad (\text{XI.3})$$

bu tenglama integrallansa:

$$k = \frac{1}{t} \ln \frac{C_0}{C} \quad (\text{XI.4})$$

hosil qilinadi,

bunda: C_0 — olingan moddaning dastlabki konsentratsiyasi;
 C — t vaqtdagi konsentratsiya.

(XI.4) tenglamadan:

$$C = C_0 e^{-kt}. \quad (\text{XI.5})$$

Agar a — dastlabki moddaning boshlang'ich mol soni (konsentratsiya), x — dastlabki moddalarning t vaqt ichidagi reaksiyaga kirishgan miqdor bo'lsa, ma'lum vaqtda (t) dastlabki moddaning miqdori ($a - x$) bo'ladi va

$$-\frac{dC}{dt} = \frac{d(a-x)}{dt} \text{ va } \frac{dC}{dt} = k(a-x).$$

Bu tenglama integrallansa:

$$k = \frac{1}{t} \ln \frac{a}{a-x}; \quad k = \frac{2,3}{t} \lg \frac{a}{a-x} \quad (\text{XI.6})$$

va (XI.6) tenglamadan:

$$x = a (1 - e^{-kt}). \quad (\text{XI.7})$$

Demak, k ning o'lchov birligi $\frac{1}{t}$, ya'ni t^{-1} (sek^{-1} , min^{-1} , soat^{-1}) bo'ladi.

Bimolekular (ikkinchi tartibli) reaksiyalar uchun:

$$\frac{dx}{dt} = k \cdot C_A C_B = k(a-x)(b-x),$$

C_A , C_B — dastlabki A va B moddalarning ma'lum t vaqtdagi konsentratsiyasi, a b esa A va B moddalarning dastlabki mol miqdori; x — dastlabki moddalarning t vaqtda reaksiyaga kirishgan miqdori; $(a-x)$ va $(b-x)$ ma'lum (t vaqtdagi) A va B moddalar miqdori. Bu tenglama integrallansa:

$$k = \frac{1}{t} \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}; \quad k = \frac{2,3}{t} \frac{1}{a-b} \lg \frac{b(a-x)}{a(b-x)}. \quad (\text{XI.8})$$

Agar dastlabki moddalar teng miqdorda, ya'ni $a = b$ olingan bo'lsa:

$$-\frac{dx}{dt} = k(a-x)^2 \quad (\text{XI.9})$$

va

$$k = \frac{1}{t} \left(\frac{1}{a-x} - \frac{1}{a} \right) \text{ yoki } k = \frac{1}{t} \frac{x}{a(a-x)}. \quad (\text{XI.10})$$

k ning o'lchami $[t^{-1}][c^{-1}]$ yoki $t^{-1} \text{ mol}^{-1}$ bo'ladi.

Uchinchi tartibli reaksiyalar uchun dastlabki olingan moddalar bir xil konsentratsiyada olinganda ($C_A = C_B = C_C$):

$$k = (C_A - x)^3 \quad (\text{XI.11})$$

$$k = \frac{1}{2t} \left[\frac{1}{(C_A - x)^2} - \frac{1}{C_A^2} \right]. \quad (\text{XI.12})$$

Ba'zan reaksiya tezligi dastlabki olingan moddalar konsentratsiyasiga bog'liq bo'lmaydi, bunda reaksiya nolinchii tartibli bo'ladi. Bunday reaksiyalar uchun:

$$K = \frac{C_A - x}{t}. \quad (\text{XI.13})$$

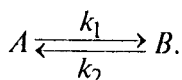
Bu xil reaksiyalar radioaktiv moddalarning parchalanishi yoki reaksiyaning tezligiga boshqa omillar ta'sir etganida (diffuziya, absorbsiya va hokazo) sodir bo'ladi.

B. Murakkab reaksiyalar

Bu xil reaksiyalarda bir vaqtning o'zida bir qancha oddiy reaksiyalar bir vaqtda yonma-yon yoki ketma-ket boradi. Reaksiyalarga qaytar, parallel, birin-ketin boruvchi reaksiyalar kiradi.

Qaytar reaksiyalar — bir vaqtda o'ngdan chapga va chapdan o'ngga boradi. Vaqt o'tishi bilan dastlabki moddalarning konsentratsiyasi (miqdori) kamayib, mahsulotlar konsentratsiyasi ko'paya boradi. Muvozanat qaror topganda o'zgarish to'xtaydi. Muvozanat qaror topgan vaqtdagi konsentratsiyalarga *muvozanat konsentratsiyalari* yoki *o'zgarmas (statsionar) konsentratsiyalar* deyiladi.

Reaksiyaning to'g'ri va teskari yo'nalishi monomolekular bo'lgan holatni ko'ramiz. Bu xil reaksiyalarni quyidagicha ifodalash mumkin:



k_1 — to'g'ri va k_2 — teskari reaksiya tezlik konstantasi. C_A , C_B lar A va B moddalar konsentratsiyasi (miqdori):

$$-\frac{dc_A}{dt} = k_1 C_A - k_2 C_B \quad (\text{XI.14})$$

yoki

$$-\frac{dx}{dt} = k_1 (a - x) - k_2 (b + x). \quad (\text{XI.15})$$

Bu tenglama integrallansa:

$$k_1 + k_2 = \frac{2,3}{t} \lg \frac{k_1 a - k_2 b}{k_1 (a - x) - k_2 (b + x)}, \quad (\text{XI.16})$$

$$k_1 + k_2 = \frac{2,3}{t} \lg \frac{y}{y - x}. \quad (\text{XI.17})$$

Bu tenglamada:

$$y = \frac{k_1 a - k_2 b}{k_1 + k_2} = \frac{Ka - b}{K - 1}. \quad (\text{XI.18})$$

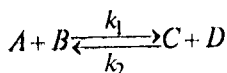
K muvozanat konstantasi bo'lib:

$$K = \frac{k_1}{k_2} = \frac{a + x_\infty}{a - x_\infty}. \quad (\text{XI.19})$$

x_∞ — reaksiya kirishgan moddaning muvozanat qaror topgandagina reaksiyaga kirishgan miqdori.

(XI. 17) tenglamadan ($k_1 + k_2$) qiymati, (XI. 19) tenglamadan k_1/k_2 ning qiymatini topib, bu tenglamani birgalikda yechib, alohida k_1 va k_2 larning qiymatlarini aniqlash mumkin.

Ilmolekular reaksiyalar. Bu xil reaksiyalarni quyidagicha sxematik ifodalash mumkin:



va reaksiya tezligi

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_2(c+x)(d+x). \quad (\text{XI. 20})$$

Agar $C_A = C_B$ baravar miqdorda olingan va reaksiya boshlanishida mahsulotlar bo'lmagan bo'lsa, $C_C = C_D = 0$:

$$\frac{dx}{dt} = k_1(a-x) - k_2x^2 \quad (\text{XI. 21})$$

va

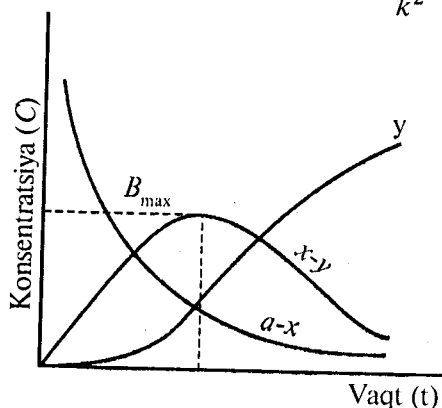
$$k_1 + k_2 = \frac{1}{t} \frac{2,3}{m_2 - m_1} \lg \frac{m_1(m_2 - x)}{m_2(m_1 - x)}. \quad (\text{XI. 22})$$

Bunda

$$m_1, m_2 = \frac{aK \pm \sqrt{K}}{K-1}, \quad (\text{XI. 23})$$

muvozanat holatda:

$$K = \frac{k_1}{k_2} = \frac{x_\infty^2}{(a - x_\infty)^2}. \quad (\text{XI. 24})$$



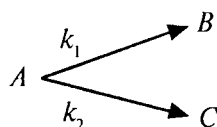
XI. 1-rasm.

Ketma-ket boruvchi reaksiyalar.

(XI.22), (XI.24) tenglamalardan ayrim k_1 va k_2 larning qiymatlarini aniqlash mumkin.

Parallel (yonna-yon) reaksiyalar. Bir vaqtda reaksiya bir qancha yo'nalishda boradi va har xil mahsulotlar hosil bo'ladi. Agar ikki yo'nalishda borib, A moddadan bir vaqtda B va C moddalar hosil

bo'lsa hamda bu ikki yo'nalish monomolekular ravishda borsa, ya'ni sxematik ravishda:



t vaqtda B moddadan x_1 va C moddadan x_2 mol hosil bo'lsa, dastlabki olingan modda (A) ning $x = x_1 + x_2$ miqdori reaksiyaga kirishadi:

$$\frac{dx}{dt} = k_1(a - x) - k_2(a - x) \quad (\text{XI. 25})$$

va

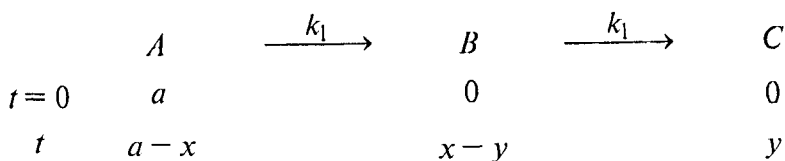
$$k_1 + k_2 = \frac{2,3}{t} \lg \frac{a}{a-x}. \quad (\text{XI. 26})$$

Ma'lum vaqtda

$$\frac{x_1}{x_2} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} = \text{const.} \quad (\text{XI. 27})$$

Bu nisbat hamma vaqt bir xil qiymatga ega bo'ladi. (XI. 26) va (XI. 27) tenglamalarni birgalikda yechib, k_1 , k_2 larning qiymatini aniqlash mumkin.

Ketma-ket boradigan — konsuketiv reaksiyalar (XI. 1-rasm). Eng oddiy ketma-ket boradigan reaksiya monomolekular reaksiya bo'lib, bu reaksiyani sxematik ravishda quyidagicha ifodalash va grafikda tasvirlash mumkin:



Agar reaksiya uchun A modddadan a mol olingan bo'lib, B , C moddalar bo'lmasa va A modddaning x moli reaksiyaga kirishgan va C modddadan y mol hosil bo'lgan bo'lsa, t vaqtda A modddadan $(a - x)$ mol, B modddadan $(x - y)$ mol qoladi. Reaksiyaning kinetik tenglamasi bo'yicha t vaqtda moddalar miqdori (konsentratsiyasi) quyidagicha bo'ladi:

$$a - x = ae^{-k_1 t} \quad x = a(1 - e^{-k_1 t}), \quad (\text{XI.28})$$

$$x - y = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} + e^{-k_2 t}), \quad (\text{XI. 29})$$

$$y = a \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]. \quad (\text{XI.30})$$

Oraliq B modddaning maksimum miqdori qaysi vaqtga to'g'ri kelishini bilish uchun (XI.29) tenglamani vaqt bo'yicha differensiallab, hosilani nolga tenglash kerak:

$$\frac{a(x-y)}{dt} = 0.$$

Shundan so'ng quyidagi tenglama olinadi:

$$t_m = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \quad (\text{XI.31})$$

yoki $k_1/k_2 = r$ deb belgilasak:

$$t_m = \frac{\ln r}{k_2(r-1)}. \quad (\text{XI.32})$$

t_m oraliq modddaning eng ko'p (maksimal) to'plangan vaqti. Oraliq B modddaning maksimal qiymati:

$$(x - y)_{\max} = \frac{ar}{1-r} \left(e^{\frac{-r \ln r}{r-1}} - e^{\frac{\ln r}{r-1}} \right) \quad (\text{XI.33})$$

bo'ladi.

XI.4. REAKSIYA TARTIBINI ANIQLASH

Reaksiya tartibini aniqlash uning mexanizmini aniqlashga yordam beradi. Reaksiya tartibi bir nechta usul bilan aniqlanadi.

1. Reaksiyaning kinetik tenglamasiga (XI. 5, XI. 8, XI. 10, XI. 12) mos kelish usuli. Reaksiya tezligi vaqt o'tishi bilan dastlabki moddaning qanchasi reaksiyaga kirishgani yoki mahsulotlardan birlashtirishining hosil bo'lgan miqdori bilan o'lchanadi.

Tajribada olingan natijalarni birin-ketin shu tenglamalarga qo'yib, tezlik konstanta (k) si qiymati hisoblab topiladi. Qaysi tenglamada hamma tajribalarda k o'zgarmasa, ya'ni bir xil qiymatga ega bo'lsa, shu tenglamaga mos tartibga ega bo'ladi.

2. Yarim ajralish vaqti usuli. Bu usulda dastlabki moddalardan har xil konsentratsiyada olib tajriba o'tkaziladi. Dastlabki moddalarning konsentratsiyasi tajriba davomida yarmi reaksiyaga kirishuviga, ya'ni yarmiga kamayishiga ketgan vaqt **yarim ajralish vaqti** deyiladi. Bu holda kinetik tenglamalarda $x = \frac{a}{2}$ bo'ladi. Agar x ning bu qiymatini kinetik tenglamalarga qo'yib, yarim ajralish vaqti ($t_{1/2}$) topilsa, quyidagi natijalar olinadi:

$$t_{1/2} = \frac{1}{2} \ln 2 \quad \text{— monomolekular reaksiyalarda;}$$

$$t_{1/2} = \frac{1}{k} \cdot \frac{1}{a} = \frac{1}{k} a^{-1} \quad \text{— bimolekular reaksiyada;}$$

$$t_{1/2} = \frac{3}{2} a^2 \quad \text{— uchmolekular reaksiyada;}$$

$t_{1/2} = \frac{1}{k_1 + k_2} = \ln \frac{2k_1}{k_1 + k_2}$ — monomolekular qaytar reaksiyada;

$t_{1/2} = \frac{\ln 2}{k_1}$ — konsuketiv reaksiyada.

$t_{1/2} = \frac{\ln 2}{k_1 + k_2}$.

Demak, oddiy va murakkab monomolekular reaksiyalarda $t_{1/2}$ qiymati reaksiya uchun qancha miqdorda modda olinganligiga qaramasdan bir xil qiymatga ega bo'lib, $t_{1/2}$ qiymati modda konsentratsiyasiga bog'liq emas. Bimolekular reaksiyada yarim ajralish vaqti olingan moddalarning konsentratsiyalari birinchi darajasiga teskari proporsional, uchmolekular reaksiyalarda modda konsentratsiyasining ikkinchi darajasiga teskari proporsionaldir. Umumiy ko'rinishda quyidagicha ifoda qilish mumkin:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)ka^{n-1}}. \quad (\text{XI.34})$$

Agar ordinata o'qiga $t_{1/2}$ ning, absissa o'qiga a ning tegishli qiymati qo'yilsa, to'g'ri chiziq hosil qilinadi.

Monomolekular reaksiya $t_{1/2}^{-a}$ koordinatasida absissalar o'qiga parallel chiziq: bimolekular reaksiyalarda $t_{1/2} = \frac{1}{a}$ koordinatalarida va uchmolekular reaksiyalarda $t_{1/2} = \frac{1}{a^2}$ koordinatalarda to'g'ri chiziq olinadi.

Agar reaksiya dastlabki moddalarning ikki xil boshlang'ich konsentratsiyasida C_1^0 , C_2^0 olib borilgan bo'lsa, ikkala holda ham

dastlabki moddalarning bir xil nisbatda ($C_1 / C_1^0 = C_2 / C_2^0$) reaksiyaga kirishgan vaqti t_1 va t_2 bo'lsa, reaksiya tartibi quyidagi formulada ifodalanadi:

$$n = 1 + \frac{\lg t_2 / t_1}{\lg C_2^0 / C_1^0}.$$

3. Differensial usul. Agar reaksiya uchun dastlabki moddalar barobar konsentratsiyada olinsa ($C_A = C_B = C_C$) va n - tartibli reaksiya borayotgan bo'lsa:

$$V = kC^n$$

va

$$\lg V = \lg k + n \lg C. \quad (XI.35)$$

Bu usulda dastlabki moddalar barobar konsentratsiyalarda bir necha marta olinadi.

Ordinatalar o'qiga $\lg V$ va absissalar o'qiga $\lg C$ qo'yilsa, to'g'ri chiziq olinadi. Bu chiziq og'ish burchagining tangensi $\operatorname{tg} \alpha = n$ bo'ladi. Bu usulni faqat oddiy reaksiyalar uchungina qo'llash mumkin.

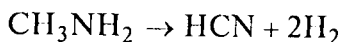
Yana bir usul bo'yicha har qaysi moddaga nisbatan reaksiya tartibi aniqlanadi va so'ng hamma olingan moddalarga nisbatan topilgan reaksiya tartiblari jamlanadi:

$$n = n_1 + n_2 + n_3 + \dots$$

va reaksiyaning umumiy tartibi topiladi. Agar uchta modda reaksiyaga kirishayotgan bo'lsa, navbatma-navbat ikki xil modda ortiqcha olinib, uchinchi modda bo'yicha reaksiya tartibi yuqoridagi usullardan foydalanib topiladi.

MASALALAR YECHISHGA DOIR MISOLLAR

1. Metilaminning vodorodsizlanish (degidrogenlash) reaksiyasi:



913 K da olib borilganda quyidagicha natijalar olingan:

t , sek	50	100	138	150	200
x , mol (reaksiyaga kirishgan modda miqdori)	0,224	0,395	0,420	0,53	0,632

Tezlik konstantasi qiymatini (k), 250 sek da metilaminning qancha miqdori (mol) reaksiyaga kirishganini, yarim ajralish vaqti ($t_{1/2}$) va reaksiya tartibini aniqlang.

Y e c h i s h . Olingan natijalar monomolekular reaksiya tenglamasi (XI.6) ga qo'yilsa:

$$t = 50, \quad k = \frac{2,3}{50} \lg \frac{1}{1-0,224} = 5,01 \cdot 10^{-3},$$

$$t = 100, \quad k = \frac{2,3}{100} \lg \frac{1}{1-0,395} = 5,01 \cdot 10^{-3},$$

$$t = 138, \quad k = \frac{2,3}{100} \lg \frac{1}{1-0,42} = 5 \cdot 10^{-3},$$

$$t = 150, \quad k = \frac{2,3}{150} \lg \frac{1}{1-0,53} = 5,02 \cdot 10^{-3},$$

$$t = 200, \quad k = \frac{2,3}{200} \lg \frac{1}{1-0,632} = 4,98 \cdot 10^{-3},$$

o'rtacha $k \approx 5 \cdot 10^{-3} \text{ sek}^{-1}$.

k ni har qaysi vaqt uchun hisoblashdan ko'ra, uning qiymati grafik usul bilan topilsa ham bo'ladi. Monomolekular reaksiya uchun

koordinataning absissa o'qiga vaqt (t), ordinata o'qiga $\lg \frac{a}{a-x}$ qiymati qo'yilsa, to'g'ri chiziq olinadi. Bu chiziqning absissa o'qiga og'ish burchagi tangensi tezlik konstantasi qiymatiga to'g'ri proporsional $k = 2,3 \lg \alpha$.

Bimolekular reaksiyalarda ham absissa o'qiga vaqt (t), ordinata o'qiga $\frac{x}{a(a-x)}$ qiymatlari qo'yib chiqilsa, to'g'ri chiziq olinadi va $k = 2,3 \lg \alpha$ ga teng bo'ladi.

250 sek da olingan moddaning qanchasi reaksiyaga kirishganligini aniqlash uchun (XI.7) tenglamadan foydalanamiz:

$$x = a(a - e^{-kt}) = 1 \left(1 - e^{5 \cdot 10^3 \cdot 250} \right)$$

$$y = e^{-kt}; \lg y = -\frac{kt}{2,3} = \frac{5 \cdot 10^{-3} \cdot 250}{2,3} - 0,544 = 1,454$$

$$y = 0,285$$

$$x = 1(1 - 0,285) = 0,715.$$

Yarim ajralish vaqtini topish uchun (XI.31) tenglamadan foydalanamiz:

$$t_{1/2} = \frac{2,3 \lg 2}{k} = \frac{2,3 \cdot 0,3}{5 \cdot 10^{-3}} = \frac{0,69}{5 \cdot 10^{-3}} = 138 \text{ sek.}$$

Reaksiya tartibini aniqlash. Tajribada olingan natijalarni monomolekular (birinchi tartibli) reaksiyaning kinetik tenglamasi (XI.6)ga qo'yib chiqqanda tezlik konstanta k hamma vaqt bir xil qiymatga ega bo'lishi, ya'ni doimo turg'un qolishi reaksiyaning birinchi tartibli reaksiya ekanligini ko'rsatadi. Agar olingan

natijalar bimolekular reaksiyaning (XI. 10) kinetik tenglamasiga

$$\text{qo'yilsa: } t = 50 \text{ sek uchun } k = \frac{2,3}{50} \cdot \frac{0,224}{1(1-0,224)} = 5,8 \cdot 10^{-3} \text{ sek}^{-1};$$

$$t = 100 \text{ sek uchun } k = \frac{2,3}{100} \cdot \frac{0,395}{1(1-0,395)} = 4,79 \cdot 10^{-3} \text{ sek}^{-1};$$

$$t = 200 \text{ sek uchun } k = \frac{2,3}{200} \cdot \frac{0,632}{1(1-0,632)} = 3 \cdot 10^{-3} \text{ sek}^{-1}.$$

k turlicha qiymatga ega. Demak, reaksiya ikkinchi tartibli emas ekan.

2. 1-misoldagi reaksiyaning tezligi mahsulotlardan biri bo'lgan vodorod bosimining o'zgarishini o'lchash orqali kuzatilgan va quyidagi natijalar olingan:

$t, \text{ sek}$	50	100	150	200
$P \cdot 10^6, \text{ N/m}^2$	0,665	1,16	1,56	1,86

298 K da tezlik konstantasi qiymatini hisoblang. Vodorod ideal gazlar qonuniga bo'ysunadi, deb faraz qilinsin.

Y e c h i s h . Gaz bosimi konsentratsiyaga to'g'ri proporsional bo'lganligidan ($p = cRT$):

$$K = \frac{2,3}{t} \lg \frac{C_0}{C} = \frac{2,3}{t} \lg \frac{a}{a-x} = \frac{2,3}{t} \lg \frac{P_0}{P_0-P}.$$

$P_0 = 2,94 \cdot 10^6 \text{ N/m}^2$, modda to'la reaksiyaga kirishganda hosil bo'lgan vodorodning bosimi.

P — vodorodning t vaqtdagi bosimi.

$$t = 50 \text{ sek.}$$

$$k = \frac{2,3}{50} \lg \frac{2,94 \cdot 10^6}{2,94 \cdot 10^6 - 1,665 \cdot 10^6} = 5,07 \cdot 10^{-3} \text{ sek}^{-1}.$$

$$t = 100 \text{ sek.}$$

$$k = \frac{2,3}{100} \lg \frac{2,94 \cdot 10^6}{2,94 \cdot 10^6 - 1,16 \cdot 10^6} = 5,02 \cdot 10^{-3} \text{ sek}^{-1}.$$

$$t = 150 \text{ sek.}$$

$$k = \frac{2,3}{150} \lg \frac{2,94 \cdot 10^6}{2,94 \cdot 10^6 - 1,56 \cdot 10^6} = 5,10 \cdot 10^{-3} \text{ sek}^{-1}.$$

$$t = 200 \text{ sek.}$$

$$k = \frac{2,3}{200} \lg \frac{2,94 \cdot 10^6}{2,94 \cdot 10^6 - 1,86 \cdot 10^6} = 4,95 \cdot 10^{-3} \text{ sek}^{-1}.$$

3. Shavel kislota $\text{H}_2\text{C}_2\text{O}_4$ ning kislotali muhitda ajralish reaksiyasi kinetikasini o'rganish uchun uning 99,5% li sulfat kislotada 1/40 m eritmasi tayyorlangan. Ma'lum vaqt oralig'ida aralashmadan 10 ml dan namuna olib, kaliy permanganat bilan titrlangan, sarflangan kaliy permanganat hajmi aniqlangan va quyidagi natija olingan:

$t, \text{ min}$	0	120	240	420	600	900	1440
Titrlash uchun ketgan kaliy permanganat hajmi — $V, \text{ ml}$	11,45	9,63	8,11	6,22	6,79	2,07	1,44

Reaksiyaning o'rtacha tezlik konstantasi va reaksiya tartibini aniqlang.

Yechish. Agar reaksiya birinchi tartibli deb faraz qilinsa,

$$k = \frac{2,3}{t} \lg \frac{C_0}{C} = \frac{2,3}{t} \lg \frac{a}{a-x}$$

tenglama bo'yicha 120 minut uchun hisoblanadi:

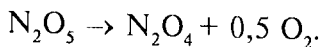
$$k = \frac{2,3}{120} \lg \frac{11,45}{9,63} = 1,44 \cdot 10^{-3} \text{ min}^{-1}.$$

Xuddi shunday, boshqa vaqtlar k uchun quyidagi qiymatlar olingan:

$$1,44 \cdot 10^{-3}; 1,44 \cdot 10^{-3}; 1,43 \cdot 10^{-3}; 1,45 \cdot 10^{-3}; 1,50 \cdot 10^{-3}; 1,40 \cdot 10^{-3}.$$

O'rtacha tezlik konstantasi $k = 1,45 \cdot 10^{-3} \text{ min}^{-1}$ ga teng hamma hollarda amalda k ning bir qiymatga ega bo'lishi, haqiqatan ham reaksiya birinchi tartibli ekanligini ko'rsatadi.

4. Gaz fazada azot (V) oksid quyidagi reaksiya bo'yicha parchalanadi:



Bu birinchi tartibli reaksiya bo'lib, 273 K da tezlik konstantasi $7,9 \cdot 10^{-7} \text{ sek}^{-1}$ ga teng. N_2O_5 ning boshlang'ich bosimi $3,04 \cdot 10^5 \text{ N/m}^2$ ga yetadi.

Qancha vaqtdan so'ng gaz aralashmasining bosimi $3,405 \cdot 10^5 \text{ N/m}^2$ (3,36 atmosfera) ga yetadi?

Y e c h i s h . Buning uchun, avvalo, qancha N_2O_5 ajralishi kerakligini bilish kerak. So'ngra (XI.7) tenglamadan foydalanib kerakli vaqtni hisoblash mumkin.

N_2O_5 to'la ajralganda aralashma bosimi 1,5 marta ortadi, chunki mol moddadan 1,5 mol modda hosil bo'layapti. x mol N_2O_5 ajralganda bosim $\frac{3,405 \cdot 10^5}{3,04 \cdot 10^5} = 1,12$ marta ortadi.

Olingan (N_2O_5) x ga nisbatan hosil bo'ladigan bosim $\left(1 + \frac{x}{2}\right)$ marta ortadi. Demak, $\left(1 + \frac{x}{2}\right) = 1,12 \text{ N / m}^2$ bo'ladi va bundan $x = 0,24$ ga teng.

Demak, bosim 1,12 marta ortishi uchun olingan N_2O_5 ning 0,24 qismi reaksiyaga kirishishi kerak, dastlabki miqdorning 0,76 qismi reaksiyaga kirishmaydi. Bunga qancha vaqt talab qilinishini aniqlash uchun (XI.5) tenglamadan foydalanamiz:

$$C = C_0 e^{-kt}.$$

Bizning misolimizda 0,76 $C = C_0 e^{-kt}$ yoki $e^{-kt} = 0,76$ va $-kt = 2,3 \lg 0,76$; $t = \frac{2,3 \lg 0,76}{k} = -\frac{2,3 \cdot 0,119}{7,9 \cdot 10^{-7}} = 3,46 \cdot 10^5 \text{ sek.}$

5. 289 K da sirka kislotasining etil efiri (etilasetat) NaOH bilan sovunlangan. Birinchi tajribada 1n etilasetatdan 1m³ olib, NaOH ning 1n eritmasidan 1m³ olib aralashtirilgan, ikkinchi tajribada NaOH ning 2n eritmasidan 1m³ olingan va quyidagi natijaga erishilgan:

$t, \text{ min}$	2	5	7	10
$a, \text{ mol}$	0,352	0,428	0,448	0,461

Reaksiyaning tezlik konstantasi va yarim ajralish vaqtini aniqlang.

Y e c h i s h : a) Birinchi tajriba bo'yicha ikkala eritmadan 1m³ olib aralashtirilganda, eritma hajmi ikki marta ko'payadi, ya'ni 2m³ bo'ldi, demak, ikkala moddaning konsentratsiyasi 0,5 n bo'ldi. (XI. 10) tenglamaga muvofiq:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}, \text{ demak :}$$

$$t = 2 \text{ min, } k = \frac{1}{2} \cdot \frac{0,352}{0,5(0,5-0,352)} = 2,380,$$

$$t = 5 \text{ min, } k = \frac{1}{5} \cdot \frac{0,428}{0,5(0,5-0,428)} = 2,38,$$

$$t = 7 \text{ min, } k = \frac{1}{7} \cdot \frac{0,448}{0,5(0,5-0,448)} = 2,420,$$

$$t = 10 \text{ min, } k = \frac{1}{10} \cdot \frac{0,461}{0,5(0,5-0,461)} = 2,375;$$

O'rtacha $k = 2,38 \text{ kmol}^{-1} \cdot \text{min}^{-1}$.

Yarim ajralish vaqti (XI.32) tenglamaga muvofiq:

$$t_{1/2} = \frac{1}{k} \cdot \frac{1}{a} = \frac{1}{2,38} \cdot \frac{1}{0,5} = 0,935 \text{ min.}$$

Tezlik konstantasining qiymati dastlabki moddalarning konsentratsiyasiga bog'liq bo'lmaganligidan 2- tajribada ham tezlik konstantasi $k = 2,38 \text{ kmol}^{-1}$ ga teng bo'ladi.

Bu tajribada eritmadagi efirning va ishqorning boshlang'ich konsentratsiyasi $C_{ef} = 0,5$, $C_{NaOH} = 1,0$. Bu tajribada moddalarning konsentratsiyasi har xil bo'lganligidan, yarim ajralish vaqti (XI.8) tenglamadan foydalanib topiladi: $t_{1/2} = \frac{2,3}{k} \cdot \frac{1}{a-b} \lg \frac{b(a-x)}{b(a-x)}$. Bunda

$x = 0,25$ ga teng. Bu qiymatlar yuqoridagi tenglamaga qo'yilsa:

$$t = \frac{2,3}{2,38} \cdot \frac{1}{1-0,5} \lg \frac{0,5(1-0,25)}{0,5(1-0,25)} \approx 3,5 \text{ min.}$$

6. 185°C da gidrazon xlorid $\text{N}_2\text{H}_5\text{Cl}$ va gidrazin N_2H_4 aralashmasida parchalanish kinetikasi $V = k[\text{N}_2\text{H}_4]^a [\text{N}_2\text{H}_5\text{Cl}]^b$ bilan

ifodalanadi. Quyidagi jadvalda keltirilgan ma'lumotlardan foydalanib, reaksiyaning tezlik konstantasini va har qaysi modda bo'yicha reaksiya tartibini toping.

Ushbu masalani yechishda quyidagi jadvaldan foydalaning.

Tezlik ($\nu \cdot 10^4$)	$[\text{N}_2\text{H}_4]$, mol/l	$[\text{N}_2\text{H}_5\text{Cl}]$, mol/l
27,7	12,65	17,8
27,4	12,50	17,8
26,1	11,60	17,8
21,9	10,00	17,8
10,5	4,80	17,8
9,86	4,51	17,8
6,48	2,96	17,8
3,57	1,71	17,0
3,31	1,71	15,9
3,40	1,71	15,7
2,58	1,71	12,25
2,29	1,71	10,9
2,21	1,71	10,55
2,19	1,71	10,4

Y e c h i s h . Yuqoridagi tenglama logarifmlansa:

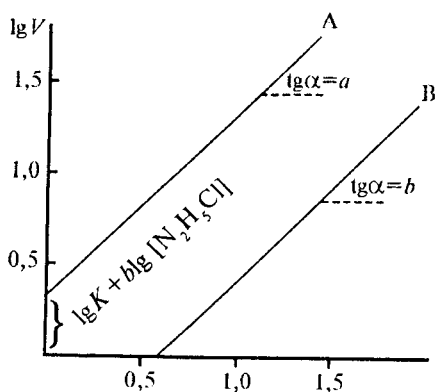
$$\lg V = \lg k + a \lg [\text{N}_2\text{H}_4] + b \lg [\text{N}_2\text{H}_5\text{Cl}].$$

Gidrazon xloridning o'zgaras konsentratsiyasida ordinata o'qiga $\lg V$, abssissa o'qiga $\lg[N_2H_4]$ qiymatlari qo'yilsa, XI.2- rasmda berilganidek, A to'g'ri chiziqli olinadi. Chiziqli abssissa o'qiga nisbatan og'ish burchagi $\operatorname{tg}\alpha = a$ bo'ladi. Chiziqli ordinata α o'qi bilan kesishgan nuqtasi $\lg k + b\lg[N_2H_5Cl]$ ga tengdir. Xuddi shunday N_2H_5Cl uchun ham $\operatorname{tg}\alpha = b$ va $\lg k + a(N_4H_4)$ B to'g'ri chizig'i hosil bo'ladi. Bu hisoblardan $n_a = n_b = 1k = 1,23 \cdot 10^{-5}$ l/mol · sek bo'ladi. Shularni e'tiborga olib,

$$K = \frac{v}{[N_2H_4][N_2H_5Cl]} = \frac{10,5 \cdot 10^{-4}}{4,8 \cdot 17,8} = 1,23 \cdot 10^{-5} \text{ l/mol} \cdot \text{sek}$$

teng bo'ladi:

7. Etilasetatning $C_1^0 = 0,01n$ eritmasi NaOH ning $C_2^0 = 0,02n$ eritmasi bilan 293 K da sovunlanganda, ularning 10% i 23 minutda reaksiyaga kirishgan. Etilasetatning bu eritmasi 0,004 n NaOH bilan sovunlanganda qancha vaqtda etilasetatning 10% i reaksiyaga kirishadi?



XI. 2-rasm.

Yechish. Olingan moddalarining konsentratsiyasi turlicha bo'lganligi uchun (XI.8) tenglamadan va birinchi tajriba ma'lumotlaridan foydalanib, k ning qiymati hisoblanadi. So'ngra yana shu tenglamadan foydalanib, ikkinchi tajriba uchun vaqt topiladi.

$\lg [N_2H_4]$, $\lg [N_2H_3Cl]$ deb belgilasak, unda

$$k = \frac{12,3}{t} \frac{1}{a-b} \lg \frac{b(a-x)}{a(b-x)}.$$

$C_1^0 = a$ va $C_1^0 = b$ deb belgilasak, unda

$$k = \frac{12,3}{t} \frac{1}{a-b} \lg \frac{b(a-x)}{a(b-x)}.$$

x ning qiymati mutanosiblik (proporsionallik) usuli bilan topiladi:

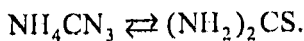
$$\left. \begin{array}{l} 0,01 \text{ ----- } 100\% \\ x \text{ ----- } 10\% \end{array} \right\} x = \frac{0,01 \cdot 10}{100} = 0,001.$$

$$\text{Demak: } k = \frac{2,3}{23} \frac{1}{0,1-0,002} \lg \frac{0,002(1-0,001)}{1(0,002-0,001)} = 3,19$$

va

$$t = \frac{1}{3,19} \frac{1}{0,04-0,004} \lg \frac{0,004(0,1-0,004)}{0,01(0,004-0,001)} = 9 \text{ min.}$$

8. Ammoniy tiosianatning tiomochevinaga aylanishi monomolekular reaksiyadir:

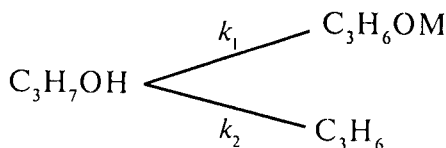


To'g'ri va teskari reaksiyalarning tezlik konstantalari 300 sek^{-1} va $k_2 = 100 \text{ sek}^{-1}$. Dastlabki aralashmada faqat ammoniy sianat bo'lgan. Qancha vaqtda ammoniy sianatning yarmi reaksiyaga kirishadi?

Yechish. Buning uchun qaytar monomolekular reaksiya-ning kinetik tenglama (XI. 16, XI. 17 va XI.33)laridan foydalanamiz. Bunda a ammoniy sianatning va b tiomochevinaning mol soni deb qabul qilsak, unda

$$t_{1/2} = \frac{2,3}{k_1 + k_2} \lg \frac{2k_1}{k_1 - k_2} = \frac{2,8}{300 + 100} \lg \frac{2300}{300 - 100} = 0,0027 \text{ sek.}$$

9. 588 K da vanadiy (VI) oksid katalizatori ishtirokida $\text{C}_3\text{H}_7\text{OH}$ (izopropilalkoxol) $\text{C}_3\text{H}_6\text{OM}$ va C_3H_6 (propilen)ga ajraladi va C_3H_8 (propan) juda kam hosil bo'lganligi uchun uni hisobga olmasa ham bo'ladi, ya'ni:



Reaksiya boshlangandan so'ng 4,3 sek o'tgach aralashma analiz qilinganda uning tarkibi mol hisobida quyidagicha bo'lgan:

$$\text{C}_3\text{H}_7\text{OH} - 27,4; \text{C}_3\text{H}_6\text{OH} - 7,5; \text{C}_3\text{H}_6 - 8,1; \text{C}_3\text{H}_8 \text{ mol.}$$

Reaksiyaning boshlanishida faqat $\text{C}_3\text{H}_7\text{OH}$ bo'lgan. k_1 va k_2 ning qiymatini aniqlang.

Yechish. Monomolekular reaksiyaning kinetik tenglamasi (XI.26) va (XI.27) lardan foydalanamiz:

$$k_1 + k_2 = \frac{2,3}{t} \lg \frac{a}{a-x} \quad \text{va} \quad \frac{k_1}{k_2} = \frac{k_1(a-x)}{k_2(a-x)}.$$

Bu tenglamani yechish uchun izopropilalkoxolning dastlabki miqdori (a)ni bilish kerak bo'ladi. $\text{C}_3\text{H}_7\text{OH}$ ning boshlang'ich miqdorini topamiz:

$$C_0 = 27,4 - 7,5 + 8,1 + 1,7 = 44,7$$

$$k = k_1 + k_2 \frac{2,3}{4,3} \lg \frac{44,7}{44,7 - (8,2 + 9,1)} = 0,115 \text{ sek}^{-1}.$$

(XI.29) tenglamaga muvofiq $\frac{k_1}{k_2} = \frac{x_1}{x_2}$ bo'lganligidan

$$\frac{k_1}{k_2} = \frac{81}{9,2} = 0,902.$$

Demak:

$$k_1 + k_2 = 0,115, \quad \frac{k_1}{k_2} = 0,902.$$

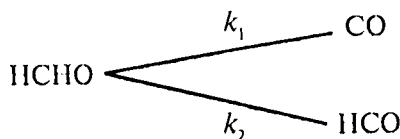
Bu ikki tenglamadan:

$$k_1 = 0,902 k_2; \quad 0,902 k_2 + k_2 = 0,115,$$

$$1,902 k_2 = 0,115; \quad k_2 = \frac{0,115}{1,902} = 0,0604 \text{ sek}^{-1},$$

$$k_1 = 0,115 - 0,0604 = 0,059 \text{ sek}^{-1}.$$

10. Aldegid nur ta'sirida reaksiyaga kirishib, bir vaqtning o'zida uchta modda — H_2 , CO , HCO hosil qilib parchalanadi. H_2 juda kam ajralib chiqishini hisobga olmaganda reaksiyani quyidagicha tasvirlash mumkin:



Ma'lum bir vaqt o'tgandan so'ng aralashmada HCO 35%ni, CO esa 65%ni tashkil qilgan. HCHO ning yarmi ajralishi uchun 410 sek talab qilingan. k_1 va k_2 ning qiymatini aniqlang.

Y e c h i s h . Masala shartida yarim ajralish vaqti $t_{1/2}$ berilgan. Uning tezlik konstantasi bilan bog'lanishi (XI.26) va (XI.27) tenglamalarda berilgan. Demak,

$$k_1 + k_2 = \frac{2,3}{t} \lg \frac{a}{a-x}.$$

Yarim ajralish vaqtida $x = \frac{a}{2}$ bo'lsa:

$$k_1 + k_2 = \frac{2,3 \lg 2}{t_{1/2}} = \frac{0,69}{410} = 1,68 \cdot 10^{-3} \text{ sek}^{-1}.$$

Ikkinchi tomondan, masala sharti bo'yicha aralashmada 35% CO va 65% HCO hosil bo'lgan. (XI.29) tenglamaga muvofiq:

$$\frac{k_1}{k_2} = \frac{35}{65} = 0,537.$$

Demak,

$$k_1 + k_2 = 1,68 \cdot 10^{-3}, \quad k_1 / k_2 = 0,537.$$

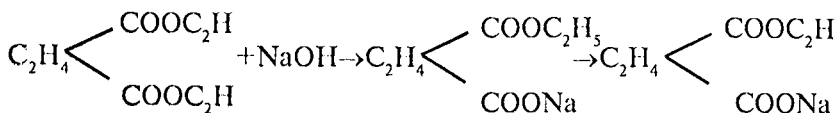
Yuqoridagi ikki tenglamadan:

$$k_1 = 0,537 k_2, \quad 0,537(k_2 + k_1) = 1,68 \cdot 10^{-3} \text{ va } k_2 = 1,09 \cdot 10^{-3} \text{ sek}^{-1}.$$

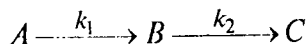
$$k_1 = 1,68 \cdot 10^{-3} - 1,09 \cdot 10^{-3} \text{ sek}^{-1} = 0,59 \cdot 10^{-3} \text{ sek}^{-1}.$$

11. Qahrabo (yantar) kislotasining dietilefiriga NaOH ta'sir ettirilganda avval qahrabo kislotasining monoetil efiri, so'ng qahrabo kislotasining natriyli o'rta tuzi hosil bo'ladi. Bular bosqich bilan boradigan reaksiyalardir.

Ya'ni:



Reaksiya NaOH ni mo'l miqdorda solgan holda olib borilgan, shunga ko'ra ikkala bosqich ham monomolekular reaksiyalar mexanizmi bo'yicha boradi:



Oraliq modda qahrabo kislotasining mononatriyli efiri (B) miqdori 103 sek dan so'ng maksimal qiymatga yetadi. Dastlabki moddaning $C_2H_4(COC_2H_5)_2$ miqdori 160 sek dan so'ng 2 marta kamaygan. k_1 va k_2 qiymatlarini aniqlang.

Yechish. Monomolekular konsektiv reaksiyaga mansub tenglamada yarim ajralish vaqti ($t_{1/2}$) dastlabki moddaning reaksiyaga kirishish tezlik konstantasi (k_1) bilan quyidagicha bog'langan:

$$t_{1/2} = \frac{2,3 \lg 2}{k_1},$$

bundan:

$$k_1 = \frac{2,3 \lg 2}{t_{1/2}} = \frac{0,69}{160} = 4,31 \cdot 10^{-3} \text{ sek}^{-1}.$$

Oraliq moddaning maksimal miqdorda bo'lish vaqtini aniqlash uchun (XI.31) tenglamadan foydalanamiz:

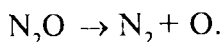
$$t_{\max} = \frac{\ln k_2 / k_1}{k_2 - k_1}; \quad 103 = \frac{2,3 \lg k_2 / 4,31 \cdot 10^{-3}}{k_2 - 4,31 \cdot 10^{-3}}.$$

Bundan:

$$k_2 = 13,0 \cdot 10^{-3} \text{ sek}^{-1}.$$

MASALALAR

1. Azot (I) oksidining ajralishi birinchi tartibli reaksiyalardir:

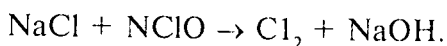


Reaksiya 900°C da borganda quyidagi natijalar olingan:

Vaqt, t (sek)	900	1800	3900	4800	7200
N ₂ O ning reaksiyaga kirishgan qismi, %	16,5	32	57	65	76

O'rtacha tezlik konstantasi va yarim ajralish vaqtini aniqlang.

2. Cl⁻ ion (NaCl) va gipoxlorid (HClO) suvli muhitda reaksiyaga kiritilgan:

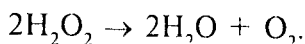


Bu reaksiyalar uchun moddalar bir xil miqdorda (mol), lekin har xil konsentratsiyada olingan. Tajribada yarim ajralish vaqti o'lchangan va quyidagi natijalar olingan:

Moddalarning dastlabki konsentratsiyasi, kmol/m ³	0,1	0,05	0,03	0,02
Yarim ajralish vaqti, sek	1,50	2,96	5,0	7,4

Reaksiyaning tezlik konstantasini va reaksiya tartibini aniqlang.

3. Vodorod peroksid suvda quyidagi reaksiya bo'yicha ajraladi:



Ma'lum miqdorda ushbu critmadan olib, kaliy permanganat bilan titrlash reaksiya kinetikasi kuzatilgan va quyidagi natijalar olingan:

Vaqt, min	0	5	10	15	20	30	40
2 sm ³ namunani titrlash uchun ketgan 0,0015 M KMnO ₄ miqdori, sm ³	23,6	18,1	14,8	12,1	9,4	5,8	3,7

Reaksiyaning o'rtacha tezlik konstantasini aniqlang.

4. 30°C da dietil efirning litiy izobutil bilan parchalanish reaksiyasi o'rganilgan, dietil efirning boshlang'ich konsentratsiyasi 4,5 mol/l va izobutillitini esa 0,15 mol/l bo'lganida quyidagi natijalar olingan:

Vaqt, min	0	1	2	3	4	5	6
Izobutillitini, mol/l	0,15	0,132	0,120	0,108	0,097	0,090	0,075

5. 3% li formaldegidning suvli eritmasida va 34,2°C da DNKning diyenaturatsiya reaksiyasining kinetikasi o'rganilgan. DNK boshlang'ich konsentratsiyasi $2 \cdot 10^{-2}$ mg/l (molekula massasi $2,8 \cdot 10^6$ ga teng) bo'lganda quyidagi natijalar olingan:

t, min	0	1	3	5	7	10	12	14	17	20
Reaksiyaga kirishmagan DNK miqdori, %	100	94,4	74,4	61,0	48,1	37,5	23,4	22,5	17,5	12,5

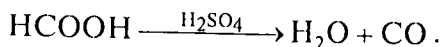
Reaksiyaning tezlik konstantasi va reaksiya tartibini aniqlang.

6. Azot (IV) oksidning yuqori haroratda ajralishi tekshirilib, quyidagi natijalar olingan:

Vaqt, sek	0	20	40	60	80	100
NO ₂ konsentratsiyasi (C), $C \cdot 10^{-11}$ mol/l	17,8	10,6	7,1	5,4	4,6	4,0

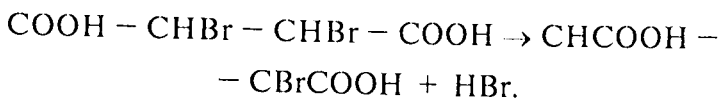
Reaksiyaning tezlik konstantasini va reaksiya tartibini aniqlang. Javobga asoslanib reaksiya tenglamasini yozing.

7. Chumoli kislotasi sulfat kislota mavjudligida quyidagi birinchi tartibli reaksiya bo'yicha ajraladi:



Reaksiya kinetikasi ajralayotgan COning miqdori (bosimi)ni o'lchash orqali kuzatilgan. Chumoli kislotaning boshlang'ich konsentratsiyasi 0,02 kmol/m³ bo'lganida yarim soatdan so'ng 5 m³ eritmadan 1,7 m³ gaz ajralib chiqqan (n.sh.). Reaksiyaning tezlik konstantasini aniqlang.

8. Dibrom qahrabo kislota isitilganda quyidagi reaksiya bo'yicha parchalanadi:



Eritma ishqor bilan titrlanganda uning titri vaqt o'tishi bilan quyidagicha o'zgargan:

t, min	0	214	380
V — ishqor, sm ³	12,11	12,44	12,68

Reaksiyaning tezlik konstantasini va qancha vaqtdan so'ng dibrom qahrabo kislotaning 1/3 qismi ajralishini hisoblab toping.

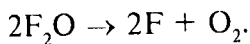
9. N-Asetilglitserinning metil efiri gidrolizi 25°C va ishqor ishtirokida o'rganilgan. Tajribada quyidagi natijalar kuzatilgan:

$t, \text{ min}$	$C \cdot 10^2, \text{ mol/l}$	$t, \text{ min}$	$C \cdot 10^2, \text{ mol/l}$
0	8,80	0,9	3,55
0,1	7,96	1,0	3,20
0,2	7,23	1,1	2,85
0,3	6,52	1,2	2,60
0,4	5,87	1,3	2,40
0,5	5,75	1,4	2,20
0,6	4,85	1,5	1,95
0,7	4,30	1,6	1,75
0,8	4,00		

Reaksiyaning tezlik konstantasi va tartibini aniqlang.

10. Reaksiyaga kirishayotgan moddaning konsentratsiyasi reaksiya boshlanganidan so'ng 10 minut o'tgach ikki barobar kamaygan. Konsentratsiya dastlabkisiga qaraganda 5 marta ko'p bo'lganida 24 sekunddan so'ng ikki marta kamaygan. Reaksiya tartibini aniqlang.

11. Ftor oksidining ajralishi:



Reaksiyaning kinetik tenglamasini quyidagicha ifodalash mumkin:

$$V = KC_{\text{F}_2\text{O}}.$$

Bu reaksiyaning tezlik konstantasi $1,04 \text{ Pa} \cdot \text{sek}^{-1}$ ga teng. Dastlabki sistema faqat F_2O dan iborat, F_2 va O_2 lar yo'q. Reaksiya

boshida sistemaning bosimi $0,067 \cdot 10^5$ Pa ga teng bo'lsa, qancha vaqtdan so'ng sistemaning bosimi $0,935 \cdot 10^5$ Pa ga yetadi?

12. $\text{CH}_2(\text{COOH}) = \text{CH}_3\text{COOH} + \text{CO}_2$ reaksiyasida bosimning o'zgarishidan foydalanib, konstantaning o'rtacha qiymatini va reaksiya tartibini aniqlang.

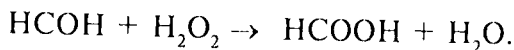
$t, \text{ min}$	0	6,5	13,0	19,9
$P \cdot 10^{-3} \text{ Pa}$	41,6	54,5	63,7	74,2

13. Bimolekular reaksiyada dastlabki moddalarning konsentratsiyasi teng holda ($C_A = C_B$) olingan. 10 minut davomida dastlabki moddalarning 25%i reaksiyaga kirishgan. Moddalarning 50%i reaksiyaga kirishishi uchun qancha vaqt kerak bo'ladi?

14. Katalizator ishtirokida 1373 K da ammiakning azot va vodorodga ajralish kinetikasi tekshirilgan. Reaksiya boshida faqat ammiak bo'lib, vodorod va azot bo'lmagan. Ammiakning yarim ajralish vaqti ammiakning boshlang'ich bosimiga quyidagicha bog'liq bo'lgan:

$P, \text{ mm sim. ust.}$	265	130	58
$t_{1/2}, \text{ min}$	7,6	3,7	1,7

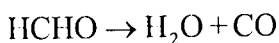
15. Chumoli kislotasining vodorod peroksid va formaldegiddan hosil bo'lish reaksiyasi quyidagicha:



Reaksiya ikkinchi tartibli. Agar ularning molar critmasidan barobar hajmda olib aralashtirilsa, 332,2 K da 2 soatdan so'ng chumoli kislotasining konsentratsiyasi 0,215 mol/l ga teng bo'ladi.

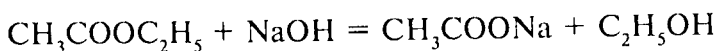
Tezlik konstantasini va dastlabki moddalarning 90% i reaksiyaga kirishishi uchun qancha vaqt kerak bo'lishini aniqlang. Agar dastlabki aralashma 10 marta suyultirilsa, dastlabki moddalarning 90% i reaksiyaga kirishishi uchun qancha vaqt kerak bo'ladi?

16. Formaldegidning gaz fazadagi ajralish reaksiyasi



ikkinchi tartibli reaksiya bo'lib, 783 K da tezlik konstantasi $2,7 \cdot 10^{-8} \text{ Pa}^{-1} \text{ sek}^{-1}$ ga teng. Reaksiya davomida bosim $0,5 \cdot 10^5 \text{ Pa}$ dan (sof formaldegidning bosimi) $0,75 \cdot 10^5 \text{ Pa}$ gacha o'zgargan. Agar bosim $1,0 \cdot 10^5 \text{ Pa}$ gacha o'zgarsa, birinchi tajribadagidek miqdorda HCHO parchalanishi uchun qancha vaqt kerak bo'ladi?

17. Sirka kislota etil efirining sovunlashish reaksiyasi

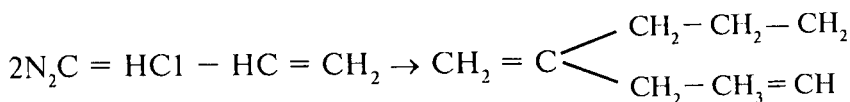


tezlik konstantasi $5,4 \text{ min}^{-1} \text{ mol/l}$ ga teng.

1) Agar efir va ishqorning konsentratsiyasi $C_{ef} = C_{ish} = 0,02 \text{ mol/l}$ va 2) ishqorning konsentratsiyasi $0,02 \text{ mol/l}$, efirning konsentratsiyasi $0,01 \text{ mol/l}$ bo'lsa, 10 minutda efirning necha foizi(%) reaksiyaga kirishadi?

18. Reaksiya bo'yicha 23°C da murakkab efir olish reaksiyasida tezlik konstantasi $2,7 \cdot 10^{-2} \text{ m}^3/\text{kmol} \cdot \text{sek}$ ga teng. Reaksiya uchun olingan moddalarning konsentratsiyasi bir xil bo'lganda yarim ajralish vaqti 400 sek bo'lsa, dastlabki moddalarning konsentratsiyasi qanchaga teng bo'ladi?

19. Butadienning gaz fazada dimerlanish reaksiyasi:



Bu ikkinchi tartibli reaksiya bo'lib, 599 K da o'tkazilgan tajribada quyidagi natijalar olingan:

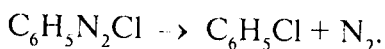
$t, \text{ min}$	$P \cdot 10^{-3}, \text{ N/m}^2$	$t, \text{ min}$	$P \cdot 10^{-3}, \text{ N/m}^2$	$t, \text{ min}$	$P \cdot 10^{-3}, \text{ N/m}^2$
0	84,2	20,78	74,2	68,05	69,9
3,25	82,4	29,18	71,4	77,57	62,0
6,12	80,9	36,38	69,5	99,05	60,4
10,08	78,9	49,30	66,4	103,58	59,0
14,30	76,8	60,87	64,4	119,00	57,7
				135,72	56,4

Grafik va analitik usul bilan tezlik konstantasining qiymatini aniqlang.

20. 0,01 n sirka kislotaning etil efiri 0,002 n NaOH bilan 23 sek da 10% ga efir sovunlangan. Shu konsentratsiyadagi efir 0,005 n NaOH bilan sovunlanganda qancha vaqtdan so'ng uning 10%i sovunlanadi? Sovunlash reaksiyasi ikkinchi tartibli reaksiya deb qaralsin.

21. FeCl_2 ning KClO_2 bilan oksidlanish reaksiyasi uchinchi tartibli reaksiyadir. Reaksiyaga olingan moddalarning dastlabki konsentratsiyalari o'zaro teng: $C_A = C_B = 0,2 \text{ mol/l}$. Agar vaqt minut va konsentratsiya mol/l bilan ifodalansa, tezlik konstantasi taxminan 1 ga teng bo'ladi. Reaksiya boshlangach necha soatdan keyin FeCl_2 ning konsentratsiyasi ikki baravar kamayadi?

22. Fenildiazoxlorid quyidagi reaksiya bo'yicha ajraladi:



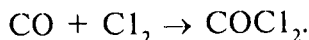
325 K va dastlabki konsentratsiyasi 10 g/l bo'lgan $C_6H_5N_2Cl$ reaksiyaga kiritilganda quyidagi natija olingan:

$t, \text{ min}$	6	9	12	14	18	22	24	26	30	∞
Ajralgan $N_2, \text{ sm}^3$	19,3	26,0	32,0	36,0	41,3	45,0	46,5	48,3	50,4	58,3

Har xil usullar bilan reaksiya tartibini va tezlik konstantasini aniqlang. Dastlabki modda 75% ajralishi uchun qancha vaqt kerak bo'ladi?

23. 583,2 K da $2CO = CO_2 + C$ reaksiyasida 30 minutdan so'ng bosim $1,049 \cdot 10^5 \text{ Pa}$ dan $0,924 \cdot 10^5 \text{ Pa}$ gacha pasaygan. Xuddi shu vaqtda $0,714 \cdot 10^5 \text{ Pa}$ dan $0,624 \cdot 10^5 \text{ Pa}$ gacha kamaygan ($V = \text{const}$). Reaksiya tartibini toping.

24. CO va Cl_2 bir xil konsentratsiyada olinib, 300 K da ($V = \text{const}$) o'zaro reaksiyaga kiritilgan:

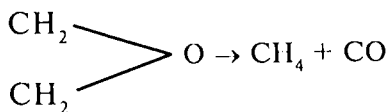


Vaqt o'tishi bilan sistemaning bosimi quyidagicha kamaygan:

$t, \text{ min}$	0	5	10	15	21
$P \cdot 10^5, \text{ Pa}$	0,963	0,900	0,829	0,779	0,735

Reaksiya tartibi nechaga teng bo'ladi?

25. Etilen oksidning parchalanish

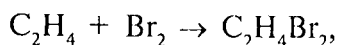


reaksiyasi 687,7 K da turg'un hajmda ($V = \text{const}$) da olib borilganda sistemaning bosimi vaqt bilan quyidagicha o'zgargan:

t, min	0	4	7	9	12	18
$P \cdot 10^5, \text{Pa}$	0,153	0,163	0,168	0,172	0,178	0,188

Tezlik konstantasini va reaksiya tartibini toping.

26. C_2H_4 va Br bir xil konsentratsiyada, lekin har xil boshlang'ich konsentratsiyada olinib, 25°C da reaksiyaga kiritilgan:



Reaksiya kinetikasi brom konsentratsiyasining kamayishini o'lchash orqali kuzatilgan. Br konsentratsiyasining ma'lum vaqtdan so'ng 2 marta kamayishi aniqlangan.

Dastlabki konsentratsiya, kmol/m^3	0,063	0,03	0,02	0,01	0,0075
Dastlabki konsentratsiya 2 marta kamaygan vaqt, sek	117000	196000	295000	500000	785000

Reaksiyaning tezlik konstantasini va tartibini aniqlang.

27. $20,5^\circ\text{C}$ da $0,02 \text{ mol/l}$ etilasetat $0,02 \text{ mol/l}$ NaOH bilan sovunlangan. Reaksiyaga kirmagan ishqorning miqdori titrlash bilan aniqlangan.

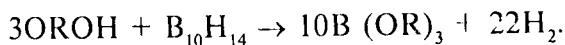
Olingan natija quyida keltirilgan:

$t, \text{ min}$	0	5	15	23	35	55	120	
Ishqor konsentratsiyasi, kmol/m^3	0,02	0,0128	0,00766	0,0054	0,00426	0,00289	0,00158	0

Reaksiyaning o'rtacha tezlik konstantasi aniqlansin.

28. Dioksan $\text{C}_4\text{H}_8\text{O}_2$ qizdirilganda ajralish reaksiyasining kinetikasi tekshirilgan. Ikki xil boshlang'ich konsentratsiyada $1,075 \cdot 10^6$ va $5,45 \cdot 10^5 \text{ Pa}$ /800 va 400 mm sim. ust. Yarim ajralish vaqti mos ravishda 13,9 va 19 min bo'lgan. Reaksiya tartibini toping.

29. 25°C da benzil eritmasida karbaron alifatik spirt bilan quyidagi stexiometrik tenglama bo'yicha reaksiyaga kirishadi:



Quyidagi ma'lumotlardan foydalanib, har qaysi modda bo'yicha reaksiya tartibini toping:

$V_0 \cdot 10^8, \text{ mol/l} \cdot \text{sek}$	$(\text{B}_{10}\text{H}_{14}), \text{ mol/l}$	$(\text{R-OH}), \text{ mol/l}$	$V_0, \text{ mol/l} \cdot \text{sek}$	$(\text{B}_{10}\text{H}_{14}), \text{ mol/l}$	$(\text{ROH}), \text{ mol/l}$
2,00	0,01	3,0	67	1,00	1,0
4,02	0,02	3,0	53	1,00	0,8
8,05	0,04	3,0	40	1,0	0,806
12,02	0,06	3,0	26	1,00	0,4
16,10	0,08	3,0	13	1,00	0,2
20,10	0,10	3,0	6,7	1,00	0,1

30. 195°C da 0,200 M lauril kislotaning 0,002 M lauril spirti $\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$ bilan efirlash reaksiyasi tekshirilib, quyidagi natijalar olingan:

$t, \text{ min}$	Reaksiyaga kirishgan, %	$t, \text{ min}$	Reaksiyaga kirishgan, %
0	0	420	57,0
15	0,20	480	59,7
30	8,50	555	61,6
60	18,5	600	62,9
120	33,1	660	64,6
180	40,7	780	66,9
240	44,7	900	69,2
300	49,7	1080	71,6
360	53,6	1320	74,1

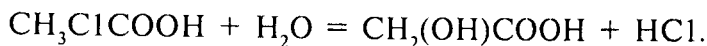
Reaksiyaning umumiy tartibini aniqlang.

31. 583,2 K da mishyak gidridi AsH_3 vodorodga va qattiq holdagi mishyakka ajraladi. Reaksiya davomida bosim quyidagicha o'zgargan (qattiq mishyak bug' bosimi hisobga olinmagan), ($V=\text{const}$).

$t, \text{ soat}$	0	5,5	6,5	8,0
$P \cdot 10^5, \text{ Pa}$	0,798	1,074	1,091	1,114

Tezlik konstantasi va reaksiya tartibini aniqlang.

32. 298 K da monoxlorsirka kislotasi suv (mol miqdorda olingan) bilan reaksiyaga kirishgan:

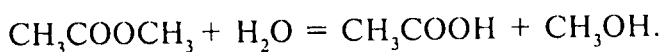


Reaksiyaning borishi eritmada namuna olinib, uni ishqor bilan titrlash orqali kuzatilgan va quyidagi natijalar olingan:

$t, \text{ min}$	0	600	780	2070
Ishqor miqdori, sm^3	12,9	15,8	16,4	20,5

Tezlik konstantasi va reaksiya tartibini aniqlang. Qancha vaqtdan so'ng uchala kislotaning miqdori tenglashadi?

33. Metilsirka efiri suvda quyidagi reaksiya bo'yicha gidrolizlanadi:

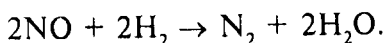


Reaksiyaning borishi eritmada ma'lum miqdorda namuna olib, ishqor bilan titrlash orqali kuzatilgan va quyidagi natija olingan:

$t, \text{ min}$	0	30	60	90	120	150
2 sm^3 namunaga ketgan 0,05n ishqorning miqdori, sm^3	12,70	13,81	16,73	15,52	16,80	20,22

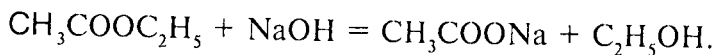
Hamma usullar bilan reaksiyaning o'rtacha tezlik konstantasini toping.

34. 298,2°C da azot (II) oksidning vodorod bilan qaytarilishi quyidagi stexiometrik reaksiya bo'yicha boradi:



Moddalar dastlab ekvivalent miqdorda ($\text{bosim } 9,454 \cdot 10^5 \text{ Pa}$) olinganda bosim 102 sek da ikki marta kamaygan. Agar bosim $0,384 \cdot 10^5 \text{ Pa}$ olinsa, 140 sek dan so'ng bosim ikki marta kamaygan. Reaksiya tartibini ($V = \text{const}$ uchun) aniqlang.

35. 298,2 K da etilsirka efiri ishqor bilan quyidagi reaksiya bo'yicha sovunlanadi:



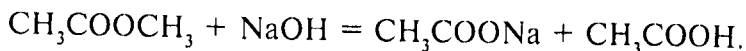
Reaksiya uchun olingan moddalarning konsentratsiyasi bir xil: $C = 0,01 \text{ g-ekv/l}$.

Reaksiyaning borishi aralashmadan ma'lum miqdordagi namunani HCl bilan titrlash orqali kuzatilgan.

$t, \text{ min}$	0	4,0	10,4	28,2	∞
0,1 sm^3 aralashmani titrlash uchun ketgan 0,001 M HCl miqdori	61,95	50,59	42,40	29,31	14,9

O'rtacha tezlik konstantasini va reaksiya tartibini toping.

36. 298,2 K da metilsirka efiri teng miqdordagi ishqor ($C = 0,01 \text{ g-ekv/l}$) bilan sovunlangan.

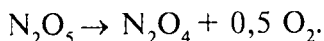


Quyidagi natijalar olingan:

$t, \text{ min}$	3	5	7	10	15	25
$C \cdot 10^3 \text{ NaOH, g-ekv/l}$	7,40	6,34	5,5	4,64	3,63	2,54

O'rtacha tezlik konstantasining qiymatini va reaksiya tartibini aniqlang.

37. Azot (V)-oksidi quyidagi reaksiya bo'yicha ajraladi:

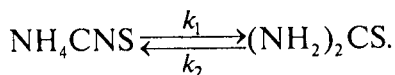


Reaksiyaning borishi turg'un hajm ($V = \text{const}$) da aralashma bosimini o'lchash orqali kuzatilgan va 328,2 K da quyidagi natijalar olingan:

t, min	3	4	5	6	7	8	9	10
Bosimning ortishi, 10^{-3} Pa	8,7	12,7	15,3	18,1	20,1	22,4	24,4	26,3
t, min	12	14	16	18	22	26	30	38
Bosim, 10^{-3} Pa	29,1	31,4	33,6	35,5	38,5	39,9	41,2	42,6

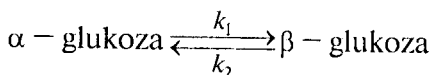
Tezlik konstantasi qiymatini, reaksiya tartibini va yarim ajralish vaqtini toping.

38. Ammoniy rodanid NH_4CNS va tiomochevinaning $(\text{NH}_2)_2\text{CS}$ bir-biriga aylanishi mono-monomolekular qaytar reaksiyadir:



Ammoniy rodanidning boshlang'ich konsentratsiyasi $0,05 \text{ kmol/m}^3$ ga teng bo'lganida tiomochevina bo'lmagan. Muvozanat qaror topganda ammoniy rodanidning konsentratsiyasi $0,01 \text{ kmol/l}$ bo'lgan. Tezlik konstantalarining nisbati k_1/k_2 ni toping.

39. Glukozaning mutarotatsiya reaksiyasi



kinetikasini tekshirish qutblanish yuzasining aylanish burchagi o'zgarishini kuzatish orqali olib borilgan. Quyida t vaqtda $a_t - a_\infty$ burchak aylanishining farqi keltirilgan. Bunda a_t — aralashmaning t vaqtdagi aylanish burchagi, a_∞ — muvozanat qaror topgandagi aylanish burchagi, $k_1/k_2 = 0,575$.

$t, \text{ min}$	0	30	60	90	125	180	220	260	300	360	450
$a_t - a_\infty$	13,01	11,86	10,84	9,88	8,87	7,49	6,61	5,83	5,16	4,28	3,23

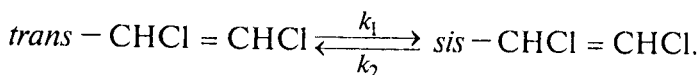
k_1 va k_2 larning qiymatini toping.

40. Ammoniy rodanid NH_4CNS ning tiomochevinaga $(\text{NH}_2)_2\text{CS}$ aylanishi mono-monomolekular qaytar reaksiyadir. Quyida keltirilgan ma'lumotlardan foydalanib, to'g'ri va teskari reaksiyalarning tezlik konstanta (k_1 va k_2) lari qiymatini hisoblab toping.

$t, \text{ min}$	0	19	38	48	60
NH_4CNS ning reaksiyaga kirishgan miqdori, %	2,0	6,9	10,4	12,3	13,6

Muvozanat qaror topganda ammoniy rodanidning konsentratsiyasi 23,2% bo'lgan.

41. Etilen dixloridning izomerizatsiyasi qaytar reaksiyadir:



Reaksiya 572 K da olib borilganda vaqt bilan trans — $\text{CHCl} = \text{CHCl}$ konsentratsiyasi quyidagicha o'zgargan:

t , sek	6	600	1080	∞
C , %	95	82,88	75,24	41,89

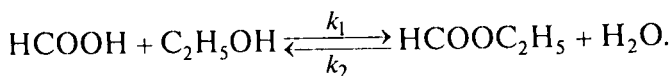
To'g'ri va teskari reaksiyalarning tezlik konstantalarini aniqlang.

42. 273 K da 73,2% etil spirti 0,677 mol HCOOH va 0,026% HCl (suv hisobga olinmaganda) aralashtirib, formiat hosil bo'lish reaksiyasi kuzatilgan va ma'lum vaqt oralig'ida aralashmadan 5 ml dan namuna olib turib $\text{Ba}(\text{OH})_2$ bilan titrlanganda quyidagi natijalar olingan:

t , min	0	50	100	160	220	∞
V , ml	43,52	40,40	37,75	35,10	31,00	24,28

Etil formiatining hosil bo'lish tezlik konstantasi k_1 , ajralish tezlik konstantasi k_2 va muvozanat konstantasi qiymatlarini aniqlang (suv va etil spirti konsentratsiyasi turg'un deb qaralsin).

43. Chumoli kislotasi etil efirining hosil bo'lishi va ajralishi monomolekular reaksiyadir:



Reaksiya 303 K da olib borilganda quyidagi natijalar olingan (kislotasi miqdori titrlash orqali aniqlangan). Reaksiyada dastlab efir bo'lmagan.

t , min	0	1700	1000	14000	200000	40000
Kislotasi miqdori, sm^3	29,44	28,59	24,77	23,03	21,28	16,80

Teskari reaksiyaning (efir ajralishi reaksiyasining) tezlik konstantasi $k_2 = 0,175 \cdot 10^{-5} \text{ min}^{-1}$. To'g'ri reaksiyaning tezlik konstantasi k_1 ni aniqlang.

44. $A \xrightleftharpoons[k_2]{k_1} B$ reaksiyasida to'g'ri va teskari reaksiyalarning

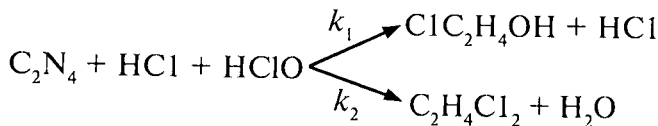
tezlik konstantasi $k_1 = 1$ va $k_2 = 15 \text{ sek}^{-1}$ ga teng. Reaksiyaga A va B moddalar bir xil olingan: $C_A = C_B = 0,02 \text{ kmol/m}^3$.

0,08 sekunddan so'ng A va B moddalarning konsentratsiyasi qanchaga teng bo'ladi?

45. $A \xrightleftharpoons[k_2]{k_1} B$ reaksiyaning muvozanat konstantasi $k = 10$.

To'g'ri reaksiyaning tezligi $k_2 = 0,2 \text{ sek}^{-1}$. Qancha vaqtdan so'ng moddalarning konsentratsiyasi tenglashadi? Reaksiya boshlanishida B modda bo'lmagan.

46. Quyidagi reaksiya parallel ravishda boradi:



Etilen ortiqcha miqdorda olingan, $k_1/k_2 = 0,314$. Konsentratsiya mol/l da olingan. 240 minutdan so'ng konsentratsiyalar o'lchanganida quyidagi natijalar olingan:

Modda	Reaksiya boshlanishida	Tajriba oxirida
$[\text{NClO}] \cdot 10^3, \text{ mol/l}$	8,675	3,695
$[\text{HCl}] \cdot 10^3, \text{ mol/l}$	0,612	0,532

Har qaysi reaksiyaning tezlik konstantasi k_1 va k_2 ni aniqlang.

47. $A \xrightarrow{k_1} B$ va $2A \xrightarrow{k_2} B$ parallel reaksiyada A kon-

centratsiyasi $0,2 \text{ kmol/m}^3$ bo'lganda ikkala reaksiyaning tezligi o'zaro teng bo'ladi. A konsentratsiya $0,4 \text{ kmol/m}^3$ bo'lganda, A ning reaksiyaga kirishish tezligi $0,24 \text{ kmol/m}^3 \cdot \text{sek}$ ga teng. k_1 va k_2 qiymatlarini toping.

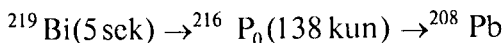
48. ABC $k_1 k_2$ parallel reaksiyada B moddaning chiqishi 63% , A moddaning yarim ajralish vaqti 19 sek . k_1 va k_2 topilsin.

49. Neftni termik krekinglash reaksiyasida benzin oraliq moddadir.

Neft $\xrightarrow{k_1}$ benzin $\xrightarrow{k_2}$ gazsimon moddalar 673 K da benzin hosil bo'lish reaksiyasining tezlik konstantasi $k_1 = 0,283 \text{ soat}^{-1}$, benzinning parchalanish reaksiyasi tezlik konstantasi $k_2 = 0,102 \text{ soat}^{-1}$ ga teng. 1 tonna neft kreking qilinganda benzinning maksimum miqdori va qancha vaqtdan so'ng bunga erishilishi mumkinligi aniqlansin.

50. $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ reaksiyasida B ning qiymati maksimumga yetganda $C_A/C_B = 4 : 5$ bo'ladi. A ning 25% miqdori reaksiyaga kirishishi uchun 85 sek vaqt kerak bo'ladi. k_1 va k_2 ning qiymatini toping.

51. Vismut²¹⁹ Bi izotopining radioaktiv parchalanishi quyidagicha boradi:



Qancha vaqtdan so'ng ^{216}Po ning miqdori maksimumga yetadi?

KO'P VARIANTLI MASALALAR

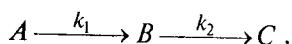
Quyidagi jadvalda keltirilgan ma'lumotlardan foydalanib, reaksiyaning vaqt bo'yicha borishi, reaksiyaning tezlik konstantasi va tartibini aniqlang.

№	Reaksiya	t, min	Reaksiyaning berilishi "a"	T, K
1	2	3	4	5
1	$2\text{NCl}_2 \rightarrow \text{N}_2 + 3\text{Cl}_2$ $a - \text{N}_2$ ning hajmi (10^{-6} , m^3) Cl_2 —yuritilgan	4 6 22 ∞	10 13 26 28,5	298,2
2	$2\text{HgCl}_2 + \text{HCOONa} \rightarrow \text{Hg}_2\text{Cl}_2 + \text{NaCl} + \text{HCl} + \text{HCO}_2$ $a - \text{HgCl}_2$ konsentratsiyasi (kmol/m^3), $b - \text{HCOONa}$ konsentratsiyasi (kmol/m^3)	0 3 0 3 0 1 1,2	b 0,1034 0,0679 0,503 0,326 0,1028 — — 0,1734 — 0,17334 — 1,0227 0,09579 0,3279	298,2
3	$\text{C}_6\text{H}_5\text{C}=\text{CCOONa} + \text{J}_2 \rightarrow \text{C}_6\text{H}_5\text{J}-\text{C}=\text{CJCOONa}$ Dastlabki moddalar ekvivalent konsentratsiyalarda olingan $25 \cdot 10^{-6} \text{ m}^3$ namunani tayyorlashga ketgan (10^{-6} m^3 da) 0,1 n sulfat eritmasining miqdori	0 29 0 34,5	24,28 8,32 21,00 7	298,2
4	$\text{Rn} \rightarrow \text{RaH}$ $a - \text{Rn}$ gazning hajmi (10^{-6} m^3)	0 70 110 140 165 200 250 360 450 600 750	a 0,102 0,062 0,044 0,033 0,025 0,019 0,016 0,007 0,003 0,002 0,000	
5	$2\text{C}_2\text{H}_5\text{OH} + 2\text{Br}_2 \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + 4\text{HBr}$ spirt ortiqcha miqdorda olingan $a - \text{bromning konsentratsiyasi}$ (10^3 , kmol/m^3)	0 4 6 10 15 0 4 10 15	a 4,24 3,14 2,49 2,24 1,78 8,14 6,10 4,46 3,73	298,2

1	2	3	4	5
6	$2\text{H}_2\text{O}_3 \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$ suv eritmasida a —namunani titrlashga ketgan KMnO_4 miqdori (10^{-6} , m^3)	0 11,5 27,1 42,5	23,89 19,30 14,50 10,99	303,2
7	$\text{K}_2\text{S}_2\text{O}_8 + 2\text{KJ} \rightarrow 2\text{K}_2\text{SO}_4 + \text{J}_2$ $a - 25 \cdot 10^{-6} \text{ m}^3$ namunani titrlashga ketgan 0,01 n $\text{Na}_2\text{S}_2\text{O}_3$ eritmasi miqdori	9 16 32 ∞	4,52 7,80 14,50 10,99	
8	N_2O_5 oksidi CCl_4 da (erituvchi) kislorod ajratib parchalanadi. $a = \text{O}_2$ hajmi (10^{-6} , m^3)	20 40 60 80 90	a 11,4 19,9 23,9 27,2 29,5	298,2
9	H_2O — katalizator ishtirokida kislorod ajratib parchalanadi. $a - \text{O}_2$ ning hajmi sm^3 (10^{-6} , m^3)	10 30 ∞	3,3 8,1 15,6	303,2
10	$\text{CH}_3\text{COOC}_2\text{H}_5\text{NaOH} = \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$ a, b efir va ishqorning dastlabki konsentratsiyalari, x dastlabki moddalarning kamayishi (kmol/m^3)	0 0 178 273 531 866 1510 1918 2401	$a-x$ $b-x$ 0,00980 — 0,00486 0,00892 — 0,00398 0,00864 — 0,00398 0,00752 — 0,00297 0,00724 — 0,00230 0,00646 — 0,00230 0,00646 — 0,00151 0,00603 — 0,00100 0,00574 — 0,00080	291,2
11	$\text{C}_{12}\text{H}_{12}\text{O}_{11} + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ c — qand $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ning ma'lum vaqtdagi konsentratsiyasi (kmol/m^3) c_0 — boshlang'ich konsentratsiya 0,65 (kmol/m^3)	0 1435 4315 7070 11360 14170 16935 19815 29925	$C_{0/c}$ 1 1,081 1,266 1,464 1,830 2,117 2,466 2,867 4,962	298,2

1	2	3	4	5
12	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} =$	0	$a-x$	293,7
	$\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$	300	0,0200	
	$a_1=b$ efir va ishqorning	900	0,0128	
	dastlabki konsentratsiyalari,	1380	0,00760	
	(kmol/m ³), x —dastlabki	2100	0,00540	
	moddalar	3300	0,00426	
	konsentratsiyalarining	7200	0,00289	
13	kamayishi (kmol/m ³)		0,00138	
		0	2,33	
		184	2,08	
		319	1,91	
	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + 0,5\text{O}_2$	526	1,67	
	$a - \text{N}_2\text{O}_5$ konsentratsiyasi	867	1,36	
	(kmol/m ³)	1198	1,11	
		1827	0,72	
		2315	0,55	
		314	0,34	

2. 298 K da ketma-ket boradigan birinchi tartibli reaksiya quyidagicha boradi:



Dastlabki A moddaning boshlang'ich konsentratsiyasi $[A]_0 \times k_1 = 0,1 \text{ min}^{-1}$. Jadvalda keltirilgan ma'lumotlardan foydalanib quyidagilarni aniqlang:

1. Oraliq modda B ning maksimal konsentratsiyasi qanday teng va unga qancha vaqtdan so'ng erishiladi?

2. Dastlabki A moddaning miqdori qancha vaqtdan so'ng $[A]_1$ ga yetadi?

3. Shu vaqtda (t_1 da) B va C moddalarning konsentratsiyasi qanday bo'ladi?

4. Qancha vaqtdan so'ng oraliq modda B ning konsentratsiyasi $[B]_1$ ga teng bo'ladi?

XI.5. REAKSIYA TEZLIGIGA HARORATNING TA'SIRI

Vant-Goffning taxminiy qoidasiga muvofiq gomogen reaksiyalarda harorat 10^0 ga oshganda reaksiya tezligi 2—4 marta (γ) oshadi, ya'ni tezlikning issiqlik koeffitsiyenti:

$$\gamma = \frac{k_{t+10}}{k_t} = 2 - 4; \quad \frac{k_{t_2}}{k_{t_1}} = \gamma^{\frac{t_2 - t_1}{10}}. \quad (\text{XI.36})$$

№	$[A]_0$, mol/l	$[A]_1$, mol/l	$[B]_1$, mol/l
1	1	0,001	0,01
2	1	0,2	0,01
3	1	0,0015	0,01
4	1	0,002	0,01
5	1,15	0,001	0,01
6	2	0,001	0,02
7	2	0,001	0,015
8	2	0,001	0,012
9	1,5	0,015	0,02
10	1,5	0,015	0,01
11	1,5	0,015	0,015
12	1,5	0,015	0,012

Harorat $n \cdot 10$ ga ortsa:

$$\frac{k_{t+n \cdot 10}}{k_t} = \gamma^n. \quad (\text{X.37})$$

Haroratning reaksiya tezligiga aniq ta'siri Arreniusning aktiv to'qnashishlar nazariyasida berilgan. Bu nazariyaga muvofiq hamma

to'qnashishlar ham reaksiya sodir bo'lishiga olib kelavermaydi, faqat effektiv to'qnashuvlarga reaksiyaga sabab bo'ladi.

Arrenius nazariyasining matematik ifodasi quyidagicha:

$$K = K_0 e^{-\frac{E}{RT}}. \quad (\text{XI.38})$$

Konsentratsiya harorat o'zgarishi bilan deyarli o'zgar-maganligidan kuzatilgan tezlik uchun ham shunday tenglama tuziladi:

$$V = V_0 e^{-\frac{E}{RT}}. \quad (\text{XI.39})$$

Bunda $V_0 = k_0 [A]^{n_1} [B]^{n_2}$.

k_0 — eksponensial kattalik, E — aktivlanish energiyasi deyiladi. Effektiv to'qnashuvda, ya'ni kimyoviy reaksiya sodir bo'ladigan to'qnashishda ma'lum minimum energiya ajralishi kerak. Bu energiya ajralib chiqishi uchun, o'z navbatida, reaksiyaga kirishuvchi moddalar ham ma'lum energiyadan kam bo'lmagan energiyaga ega bo'lishlari kerak. *Effektiv to'qnashish sodir bo'lishi uchun reaksiyaga kirishuvchi moddalarning dastlabki energiyasiga qo'shimcha beriladigan energiya aktivlanish energiyasi (E) bo'ladi.*

(XI.38) tenglama T_1 va T_2 harorat uchun (T_2, T_1) logarifm-lansa:

$$\left. \begin{aligned} \lg k_1 &= \lg k_0 - \frac{E}{2,3R} \cdot \frac{1}{T_1} \\ \lg k_2 &= \lg k_0 - \frac{E}{2,3R} \cdot \frac{1}{T_2} \end{aligned} \right\} \rightarrow \lg \frac{k_2}{k_1} = \frac{E}{2,3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

yoki

$$\lg \frac{k_2}{k_1} = \frac{E}{2,3R} \cdot \frac{T_1 - T_2}{T_1 \cdot T_2}$$

va

$$E = \frac{2,3 \cdot R \cdot \lg k_{T_2} / k_{T_1}}{\frac{1}{T_1} - \frac{1}{T_2}}. \quad (\text{XI.40})$$

To'qnashishda reaksiya sodir bo'lishi uchun E mavjud bo'lishi bilan bir qatorda, to'qnashuvchi molekulalar fazoda bir-biriga nisbatan ma'lum ravishda joylangan (oriyentatsiya) bo'lishi kerak.

Shunday qilib:

$$k = \rho z e^{-E/RT}, \quad v = \rho z e^{-E/RT}; \quad k_0 = \rho z, \quad (\text{XI.41})$$

z — vaqt va hajm birligidagi effektiv to'qnashishlar soni (z_0 — umumiy to'qnashishlar soni). Bolsman qonuniga muvofiq, E va E dan ortiq energiyaga ega bo'lgan molekulalarning to'qnashishlar soni:

$$z = z_0 e^{-E/RT}, \quad (\text{XI.42})$$

z — molekulalar orasida vaqt birligidagi to'qnashishlar soni ikkita bir xil gaz molekulalari uchun:

$$z_{AA} = \frac{1}{2} \sqrt{2\pi} (2r_A)^2 \sqrt{\frac{8RT}{\pi M}} n^2, \quad (\text{XI.43})$$

bunda: r — molekula radiusi $r = 0,665 \cdot 10^{-8} \left(\frac{m}{d}\right)^{\frac{1}{3}}$; M — molekular massa; d — moddaning zichligi; k — Bolsman doimiysi ($k = \frac{R}{T} = 13,809 \cdot 10^{-24} \text{ J / grad}$); R — universal gaz doimiysi; N — Avogadro soni; n — molekulalar soni.

Ikkita har xil molekula (A va B) uchun:

$$z_{AB} = \pi n_A n_B (r_A + r_B)^2 \sqrt{\frac{8KT(M_A + M_B)}{\pi(M_A \cdot M_B)}} \text{ sm}^3/\text{molekula} \cdot \text{sek.}$$

$M = \frac{M_A \cdot M_B}{M_A + M_B}$ ga keltirilgan massa deyiladi.

z_0 — to'qnashishlar soni bo'lib, bir xil molekula uchun:

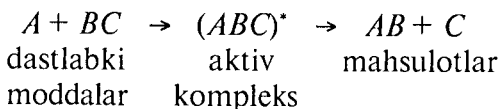
$$z_0 = \frac{1}{2} \sqrt{2} \cdot \pi d^2 \sqrt{\frac{8RT}{\pi M}}. \quad (\text{XI.44})$$

z_0 — har xil molekulalar uchun: $z_0 = \left(\frac{d_A + d_B}{2}\right) \sqrt{\frac{8KT}{n} \frac{M_A + M_B}{M_A \cdot M_B}}$

va

$$k = \rho z_0 e^{-E/RT}; V = \rho z_0 e^{-E/RT} n_A \cdot n_B. \quad (\text{XI.45})$$

O'rta holat (yoki aktiv kompleks) usuli. Bu usul bo'yicha reaksiya davomida dastlabki moddalardan iborat aktiv oraliq modda (kompleks) hosil bo'ladi, so'ng aktiv kompleks mahsulotlarga ajraladi. Reaksiyaning tezligi aktiv kompleks hosil bo'lish tezligiga teng bo'ladi. Bu usul bo'yicha reaksiyaning borishini quyidagicha sxematik ravishda ifodalash mumkin:



Aktiv kompleks usuli (nazariyasi) aktiv to'qnashishlar nazariyasi (usulini) kamchiligini to'ldiruvchi va reaksiya mexanizmini to'laroq tushuntirib beruvchi, ya'ni oydinlashtiruvchi usuldir.

Aktiv kompleks usulining asosiy kinetik tenglamasi quyidagilardir:

$$K = \frac{RT}{h} e^{-\frac{\Delta F^*}{RT}}$$

va

$$\begin{aligned} \Delta F^* &= \Delta H^* - T \Delta S^* \\ \Delta S^* &= \frac{\Delta H^* - \Delta F^*}{T} \end{aligned}$$

bo'lganligidan

$$K = e^{\frac{RT}{h}} e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \quad (\text{XI.46})$$

$$K = e^{\frac{RT}{h}} e^{\Delta S^*/R} \cdot e^{-E/RT} \quad (\text{XI.47})$$

$$k_0 = \rho z = e^{\frac{RT}{h}} e^{\Delta S^*/R} \quad (\text{XI.48})$$

$$E = \Delta H^* + RT, \quad (\text{XI.49})$$

k — Bolsman doimiysi = $1,38 \cdot 10^{-16}$ erg/grad, h — Plank doimiysi = $6,62 \cdot 10^{-27}$ erg · sek; R — universal gaz doimiysi.

l — transmission koeffitsiyent dastlabki moddalarning energiya g'ovini, aktiv kompleks potensali yengishini tavsiflovchi miqdor — dastlabki moddalarning qancha ulushi bu g'ovni yenga olishini ko'rsatadi. Amaliy hisoblarda $l = 1$ deb qabul qilingan ΔF° , ΔH° , ΔS° aktiv kompleks hosil bo'lishida Gelmgols funksiyasi, issiqlik effekti va entropiya o'zgarishi ΔF° , ΔH° , ΔS° lar standart aktivlanish entalpiyasi va standart aktivlanish entropiyasi yoki qisqa qilib, standart kattaliklar deb ham ataladi.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. Reaksiyaning harorat koeffitsiyenti $\gamma = 3,5$. 15°C da tezlik konstanta $0,2$ sek, 40°C da tezlik konstantasi qanchaga teng?

Yechish. Vant-Goff qoidasiga muvofiq (XI.36) va (XI.37) tenglamalar:

$$\frac{k_{15+25}}{k_{15}} = \gamma \frac{25}{10} = 3,5^{2,5}$$

$$k_{40} = 3,5^{2,5} \cdot k_{15} = 3,5^{2,5} \cdot 0,2 = 4,6 \text{ sek}^{-1}.$$

2. Reaksiyaning tezlik konstantasi $T_1 = 300 \text{ K}$ da $0,02 \text{ sek}^{-1}$ ga, $T_2 = 350 \text{ K}$ da esa $0,6 \text{ sek}^{-1}$ ga teng. Aktivlanish energiyasi va Arrenius tenglamasida eksponensial oldidagi kattalikni aniqlang.

Yechish. 1-usul. a) Arrenius tenglamasiga muvofiq k_0 ning qiymatini aniqlash uchun, avvalo, E ning qiymatini bilish kerak.

a) Arrenius (XI.40) tenglamasidan:

$$E = \frac{2,3R \cdot \lg k_2 / k_1}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{2,3 \cdot 8,31 \cdot 10^3 \lg \frac{0,6}{0,02}}{\frac{1}{300} - \frac{1}{350}} = 59400 \text{ kJ/mol} = 59,4 \text{ kJ/kmol}.$$

b) Tenglama (XI.40) ga muvofiq:

$$\lg k_1 = \lg k_0 - \frac{E}{2,3R} \cdot \frac{1}{T_1},$$

bundan

$$\lg k_0 = \lg k_1 \frac{E}{2,3R} \cdot \frac{1}{T} = \lg 0,02 + \frac{59400}{2,3 \cdot 8,31 \cdot 10^3} \cdot \frac{1}{300} = 4,4 \cdot 10^3.$$

2-usul — grafik usul. b) Berilgan ma'lumotlar asosida $\lg k - \frac{1}{T}$ koordinatalarida, ya'ni absissalar o'qiga $\frac{1}{T}$ va ordinatalar o'qiga $\lg k$ qiymatlari qo'yib chiqiladi. Arrenius tenglamasidan:

$$\lg k = \lg k_0 - \frac{E}{2,3k} \cdot \frac{1}{T}.$$

Bu to'g'ri chiziq tenglamasi bo'lib, to'g'ri chiziqning og'ish burchagi tangensi ($\operatorname{tg} \alpha$):

$$\operatorname{tg} \alpha = \frac{E}{2,3R}$$

ga teng.

Bundan

$$\begin{aligned} E &= 4,575 \operatorname{tg} \alpha = 4,575 \frac{\Delta \lg k}{\Delta \frac{1}{T}} = 4,575 \cdot \frac{a}{b} = 4,575 \cdot 1,43 \cdot 200 = \\ &= 13400 \text{ kal} = 56100 \text{ J.} \end{aligned}$$

Ekspontensial son (k_0) ni topamiz.

Yuqoridagi to'g'ri chiziq tenglamasini quyidagicha yozish mumkin:

$$\lg k = \lg k_0 - \operatorname{tg} \alpha \frac{1}{T} \cdot 10^{-3} = \lg k_0 - 1,43 + 200 \cdot 3,4 \cdot 10^{-3} = \lg k_0 - 9,73.$$

$$\lg k_0 = \lg k + 9,73 = 3,88 + 9,73 = -3 + 0,88 + 9,73 = 7,61; \quad k_0 = 4,1 \cdot 10^7.$$

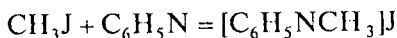
Absissalar o'qidagi ma'lum qiymat ordinatalar o'qiga to'g'ri keladigan nuqta $\lg k$ ning qiymatini ko'rsatadi. Masalan, $\frac{1}{T} = \frac{1}{503} = 3,3 \cdot 10^{-7}$ to'g'ri kelgan $\lg k = 2,177$ bo'ladi.

$$\lg k = \lg k_0 - \operatorname{tg} \alpha \cdot \frac{1}{T} = \lg k_0 - 1,43 \cdot 200 \cdot 3,3 \cdot 10^{-7} = -\lg k_0 - 9,438;$$

$$\lg k_0 = 2,177 + 9,438 = 7,61 \text{ kJ}.$$

$$k_0 = Pz_0 = 4,1 \cdot 10^{-7} \text{ l./mol} \cdot \text{min}^{-1} = \frac{4,1 \cdot 10^{-7}}{6,06 \cdot 10^{23}} = 1,13 \cdot 10^{-15} \text{ sm}^3/\text{sek}.$$

3. Metil yodid va piridin orasidagi reaksiya kinetikasi



tekshirilganda quyidagi natijalar olingan:

T K	298,2	303,2	313,2	323,2
$k \cdot 10^2 \text{ l/mol}^{-1} \text{ sek}^{-1}$	0,713	1,50	3,5	5,89

Bu ikkinchi tartibli qaytmas reaksiyadir. Piridinning zichligi $d_n = 0,98$ va metil yodidning zichligi $2,28 \text{ g/sm}^2$ ga teng bo'lsa: a) aktivlanish energiyasi va b) sterik faktorni hisoblab aniqlang.

Y e c h i s h . k_0 ning qiymatini topish uchun Arrenius tenglamasiga muvofiq E ni bilish kerak. Shunga ko'ra, oldin E , so'ng esa k_0 aniqlanadi. E ni ikki xil usul bilan topish mumkin.

a) (XI.40) tenglamaga muvofiq:

$$E = \frac{2,3R \lg k_2 / k_1}{\frac{1}{T_1} - \frac{1}{T_2}}.$$

Bu tenglamadan: $T_1 = 303,2 \text{ K}$ va $T_2 = 323,2 \text{ K}$ uchun:

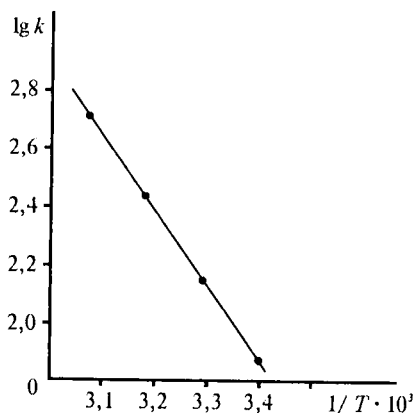
$$E = \frac{2,3R \lg k_2 / k_1}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{2,3 \cdot 8,10^3 \cdot \lg \frac{589 \cdot 10^{-2}}{1,5 \cdot 10^{-2}}}{\frac{1}{303,2} - \frac{1}{393,2}} = 13500 \text{ kal} =$$

$$= 13500 \cdot 4,187 = 54689 = 54,689 \text{ kJ}.$$

Arrenius tenglamasidan:

$$\lg K = \lg K_0 \frac{E}{2,3R} \cdot \frac{1}{T}.$$

Bu to'g'ri chiziq (XI. 3-rasm) tenglamasi bo'lib, koordinata-ning abssissalar o'qiga $\frac{1}{T}$ va ordinatalar o'qiga $\lg k$ qiymatlari qo'yilsa, to'g'ri chiziq hosil qilinadi va bu to'g'ri chiziqlarning abssis-



XI. 3-rasm.

salar o'qiga og'ish burchagi tangensi ($\operatorname{tg} \alpha$): $\operatorname{tg} \alpha = \frac{E}{2,3R}$ ga teng

bo'ladi. Bundan:

$$\begin{aligned} E &= 2,3R \operatorname{tg} \alpha = 4,573 \frac{\Delta \lg k}{\frac{1}{T}} = \\ &= 4,573 \frac{a}{b} = 4,573 \cdot 1,43 \cdot 200 = \\ &= 1340 \text{ kal} = 54,689 \text{ kJ}. \end{aligned}$$

b) Sterik faktor (P) ni aniqlash:

$$k_0 = k_0 e^{-E/RT} = P_{Z_0} e^{-E/RT}$$

yoki

$$\lg k = \lg k_0 - \operatorname{tg} \alpha \cdot \frac{1}{T} \cdot 10^3 = \lg(P_{Z_0}) - 2,861/T \cdot 10^3.$$

Demak, to'g'ri chiziqdagi istalgan nuqtani, masalan:

$$\frac{1}{T} \cdot 10^3 = 3,40 \text{ da } \lg k = 3,88 \text{ ga teng, demak,}$$

$$\lg(P_{Z_0}) = 3,88 + 2,86 \cdot 3,40 = 3,88 + 9,73 = 7,61$$

$$\text{va } p_z = 4,1 \cdot 10^7 \text{ l} \cdot \text{mol}^{-1} \text{ min}^{-1} = \frac{4,1107}{600021013} = 1,13 \cdot 10^{-15} \text{ sm}^3 \cdot \text{sek}^{-1}.$$

Shunga ko'ra, P ning qiymatini hisoblab topish uchun Z_0 ni bilish kerak bo'ladi.

(XI.44) tenglamaga muvofiq:

$$Z_0 = \frac{\sqrt{2}}{2} \pi (r_A + r_B) 2 \sqrt{\frac{8nT}{\pi}} \cdot \frac{M_A + M_B}{M_A \cdot M_B}$$

(k_0 qiymatida $n = 1$ teng bo'ladi). M_0 — piridinining molekular massasi $M_n = 79$, metil yodidning molekular massasi $M_m = 142$ ga tengligidan:

$$\frac{M_A \cdot M_B}{M_A + M_B} = \frac{79 \cdot 142}{79 + 142} = 50,7.$$

$r_A + r_B$ lar (piridin va metil yodid molekulaning radiusi) quyidagi tenglamadan topiladi:

$$r = \sqrt[3]{1,41 \cdot 1,661027 \frac{M}{d}} = 0,665 \cdot 10^{-8} \left(\frac{M}{d} \right)^{\frac{1}{3}}$$

$\pi(r_A + r_B)^2 = \delta$ ga to'qnashish kesimi deyiladi, demak:

$$\delta = 1,39 \cdot 10^{-16} \left[\frac{MA}{dA} \right]^{\frac{1}{2}} + \left[\frac{MB}{d\Delta} \right] = 1,39 \cdot 10^{-16} \left[\frac{79}{0,98} \right]^{\frac{1}{2}} + \frac{142}{2,28} = 9,5 \cdot 10^{-15} \text{ sm}^2.$$

O'rtacha tezlik:

$$\bar{u} = \sqrt{\frac{8KT}{\pi M}} = \sqrt{\frac{8,1538 \cdot 10^3 \cdot 308}{3,14 \cdot 50,7}} = 3,5810^4 \text{ sm/sek}.$$

Agar bu qiymatlar yuqoridagi tenglamaga qo'yib chiqilsa:

$$Z_0 = 3,58 \cdot 10^4 \cdot 9,5 \cdot 10^{-15} = 3,4 \cdot 10^{-10} \text{ sm}^3/\text{sek}.$$

Demak:

$$P = \frac{1,13 \cdot 10^{-15}}{3,4 \cdot 10^{-10}} = 3,31 \cdot 10^{-6}.$$

4. 1 kmol vodorod yodidning parchalanishi 566,2K da olib boriladi. Reaksiya bimolekular bo'lib, aktivlanish energiyasi $E = 1848 \cdot 10^2 \text{ J/mol}$. HJ molekulasi diametri $3,5 \cdot 10^{-10} \text{ m}$ ga teng. Vodorod yodidning konsentratsiyasi 1 kmol/m^3 . 566,2 K dagi tezlik konstantasining qiymatini hisoblab toping.

Y e c h i s h . (XI.38) va (XI.46) tenglamalarga muvofiq:

$$k = k_0 e^{-E/RT} = P Z_0 e^{-E/RT}.$$

Demak, k ni aniqlash uchun $k_0 = P Z_0$ bilish kerak, ya'ni vaqt va hajm birligi (sm^3/sek) da sodir bo'lgan effektiv to'qnashishlar sonini bilish kerak. Buning uchun umumiy to'qnashishlar sonini, so'ngra Bolsmaning taqsimot qonuni asosida effektiv to'qnashishlar sonini hisoblab topish kerak bo'ladi.

(XI.43) tenglamaga muvofiq umumiy to'qnashish soni (z) 1 sm^3 dagi molekular soni (N) teng:

$$N = \frac{6,02 \cdot 10^{23}}{10^3} = 6,02 \cdot 10^{20}$$

$$z = \frac{\sqrt{2}}{2} \pi (2r)^2 \sqrt{\frac{8RT}{\pi M^*}} = \frac{\sqrt{2}}{2} \cdot 3,14 (3,5 \cdot 10^{-10})^2 \sqrt{\frac{8,8138 \cdot 10^3 \cdot 566,2}{3,14 \cdot 0,12812}} \times \\ \times 6,02 \cdot 10^{20} = 4,25 \cdot 10^{31}.$$

1 sekundda 1 m³ hajmda to'qnashgan molekularlar sonini mol orqali ifoda qilish uchun bu sonni Avogadro soniga bo'lish va 10⁶ ga ko'paytirish kerak bo'ladi.

Aktiv molekularlar soni:

$$\frac{Z_{\text{akt}}}{Z_{\text{umum}}} = e^{-E/RT} = e^{-\frac{1848 \cdot 10^2}{8,31 \cdot 10^3 \cdot 566}} = 8,42 \cdot 10^{-18}.$$

To'qnashgan molekular soni to'qnashishlar soni z ga qaraganda ikki marta ko'p:

$$PZ_0 = 4,25 \cdot 10^{31} \cdot 12 = 8,5 \cdot 10^{31}.$$

1 sm va 1 sekundda to'qnashishlar sonini 1 sm³ dagi mol soni orqali ifodalash uchun yuqorida olingan sonni Avogadro soniga bo'lish kerak:

$$PZ_0 = 8,5 \cdot 10^{31} / 6,02 \cdot 10^{23} = 1,41 \cdot 10^7.$$

Olingan bu qiymatlar Arrenius tenglamasiga qo'yilsa, quyidagini hosil qilamiz:

$$k = PZ_0 e^{-E/RT} = 1,41 \cdot 10^7 \cdot 8,42 \cdot 10^{-18} = 11,9 \cdot 10^{-11} \text{ sm}^2 \cdot \text{mol}^{-1} \cdot \text{sek}^{-1}$$

5. Azot (II) oksidning ajralish reaksiyasining



1620 K da tezlik konstantasi $k_1 = 0,0108 \text{ mol/l} \cdot \text{sek} \cdot \text{atm}^2$, 1525 K da $k_2 = 0,0030 \text{ mol/l sek} \cdot \text{atm}^2$ ga teng. 1572 K dagi ΔH° va ΔS° ning qiymatlarini aniqlang.

Yechish. (XI.47) tenglama logarifmlansa va T 1/ R bilan almashtirilsa ($T = \frac{PV}{R}$, $P = 1 \text{ atm}$, $V = 1 \text{ m}^3$ bo'lsa), $T = \frac{1}{R}$ teng bo'ladi:

$$\lg k = \lg \frac{k}{hR} + \frac{1}{2,3R} \left(\Delta S^* - \frac{\Delta H^*}{T} \right).$$

Bolsman doimiysi $k = 1,3805 \cdot 10^{-23}$ J/grad, $h = 6,6238 \cdot 10^{-34}$ J · sek, $R = 8,3146$ J/mol · grad. ga teng:

$$\lg k = \frac{1,3805 \cdot 10^{-23}}{6,6238 \cdot 10^{-34} \cdot 0,08206} = \lg 2,5398 \cdot 10^{11} = 11,4048.$$

Yuqoridagi tenglamani 1620 K uchun yozamiz:

$$\lg 0,0108 = -1,96658 = 11,4048 + \frac{\Delta S^*}{19,147} - \frac{\Delta H^*}{19,147 \cdot 1525}$$

$T = 1525$ K uchun:

$$\lg 0,0030 = -2,52288 = 11,4048 + \frac{\Delta S^*}{19,147} - \frac{\Delta H^*}{19,147 \cdot 1525}.$$

ΔS^* va ΔH^* qiymatini aniqlash uchun quyidagi

$$\frac{\Delta H^*}{31018,4} - \frac{\Delta S^*}{19,147} = 13,37138$$

$$\frac{\Delta H^*}{29199,17} - \frac{\Delta S^*}{19,147} = 13,92708$$

tenglamalar birgalikda yechilsa, ΔS^* va ΔH^* larni topish mumkin. $\Delta S^* = 85,038$ J/mol · grad, $\Delta H^* = 276993,62$ J/mol 1525 K va 1620 K oralig'ida bu qiymatlar amaliy o'zgarmaydi.

6. Gemoglobinning denaturatsiya reaksiyasi tezlik konstantasi $T_1 = 275,2$ K da $k_1 = 2,0 \cdot 10^{-5}$ sek⁻¹ ga, $T_2 = 301,2$ K da $k_2 = 1,5 \cdot 10^{-4}$ sek⁻¹ ga teng. ΔH^* va ΔS^* qanchaga teng?

Yechish. (XI.46) tenglamani T_1 va T_2 harorat uchun yozamiz:

$$a) \quad k_1 = l \frac{kT_1}{h} e^{\Delta S^*/R} e^{-\frac{\Delta H^*}{RT_2}},$$

$$b) \quad k_2 = l \frac{kT_2}{h} e^{\Delta S^*/R} e^{-\frac{\Delta H^*}{RT_2}}.$$

Bu tenglamalarni logarifmlab, (b) tenglamani (a) tenglamaga bo'lsak:

$$\ln \left(\frac{k_2/T_2}{k_1/T_1} \right) = \frac{\Delta H^*}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

yoki

$$\Delta H^* = \frac{R \ln \frac{k_2 T_1}{k_1 T}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{2,3 R \frac{k_2 T_1}{k_1 T}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{2,3 \frac{1,5 \cdot 10^{-4}}{301} / \frac{2 \cdot 10^{-5}}{275}}{\frac{1}{275,2} - \frac{1}{301,2}} = 12 \text{ kkal/mol.}$$

ΔS^* qiymatini topish uchun $\Delta S^* = \frac{\Delta H^* - \Delta F^*}{T}$ dan foydalanib, ΔS^* ni topish mumkin. Lekin buning uchun F^* ning qiymatini bilish kerak.

ΔF^* ni topish uchun esa (XI.46) tenglamadan foydalanamiz:

$$k = e^{\frac{kT}{n}} e^{-\Delta F^* / RT}.$$

Logarifmlab ΔF^* ning qiymatini topamiz:

$$\Delta F^* = RT \ln HT/kh$$

$$\Delta S^* = \frac{\Delta H - \Delta F^*}{T} = \frac{\Delta H^* - 2,3 RT \lg k}{T}.$$

Agar bu tenglamani 301,2°C uchun yechsak, quyidagini hosil qilamiz:

$$\Delta S^* = -3,63 e \cdot \text{grad} = -36,3 \cdot 10^{-7} \text{ J/grad}.$$

7. Gidrazinning (N_2H_4) malaxit yashili bilan gidrolizini o'rganib, quyidagi natijalar olingan:

$t^\circ \text{C}$	7	14,8	23,8	30,0	38,4
$k, \text{mm}^{-1} \cdot \text{min.}^{-1}$	1060	1580	2480	3750	46,80

Aktivlanish entropiyasi (ΔS^*) va standart aktivlanish entalpiyasi (ΔH^*) qiymatini toping:

$l = 1$ ga teng deb qaralsin.

Yechish. (XI.46) tenglamani quyidagicha yozish mumkin:

$$\frac{k}{T} = l \frac{k}{h} e^{\Delta S^* / R} e^{-\Delta H^* / RT}$$

yoki $\lg \frac{k}{T} = \text{const} - \frac{\Delta H^*}{2,3 RT}$. Demak, $\lg \frac{k}{T} - \frac{1}{T}$ koordinatalarida to'g'ri chiziq olinadi (XI.4-rasm) va absissa o'qiga og'ish burchagi tangensi $\text{tg} \alpha = \frac{\Delta H^*}{2,3 R}$ ga teng bo'ladi:

$$\Delta H^* = 2,3Rtg\alpha = 7,96 \frac{\text{kcal}}{\text{mol}} =$$

$$= 3,333 \cdot 10^3 \text{ J/mol}$$

$$\Delta F^* = \Delta H^* - T\Delta S^* \text{ e } \Delta S^* =$$

$$= \frac{\Delta H^* - \Delta F^*}{T}$$

Shunga ko'ra, ΔS^* ni aniqlash uchun ΔF^* ni bilish kerak. Buning uchun (XI.46) tenglamadan foydalaniladi:

$$k = l \frac{RT}{h} e^{\Delta F^* / RT}$$

Bu tenglamadan ΔF^* ni aniqlaymiz:

$$\Delta F^* = RT \ln^{RT/h}$$

25°C uchun mazkur tenglama yechilsa,

$$\Delta F^* = 0,593(29,2 - \ln k)$$

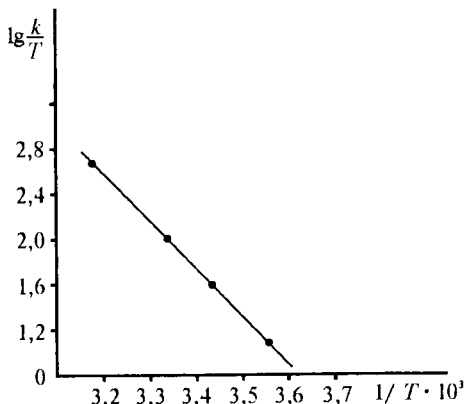
topiladi.

Endi yuqoridagi tenglamadan, ya'ni:

$$\Delta S^* = \frac{\Delta H^* - \Delta F^*}{T} \text{ dan}$$

ΔS^* aniqlanadi:

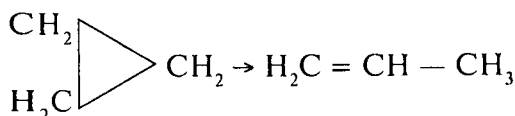
$$\Delta S^* = -24,3 \text{ e } s = 12,56 \cdot 10^4 \text{ J/mol.}$$



XI.4-rasm.

MASALALAR

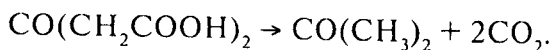
52. Siklopropanning desikllanishi (halqaning ochilishi):



Reaksiya harorati 750 K dan 800 K ga oshirilganda reaksiya tezligi 14,5 marta ortadi. Harorat ko'effitsiyentini aniqlang.

53. α glukoza ning β glukoza ga o'tish reaksiyasining harorat ko'effitsiyenti 273 — 328 K chegarasida 3,6 ga teng. Reaksiya tezligi 25 marta ortishi uchun haroratni qanchaga ko'tarish kerak?

54. Asetondikarbon kislotaning ajralish reaksiyasi:



Bu reaksiya birinchi tartibli bo'lib, $T_1 = 273,2$ K da $k = 2,46 \cdot 10^{-5} \text{ min}^{-1}$, $T_2 = 313,2$ K da $k_2 = 5,76 \cdot 10^{-3} \text{ min}^{-1}$ ga teng, $T_1' = 323,3$ K da kislotaning 70%i qancha vaqtda reaksiyaga kirishadi?

55. $A \rightarrow B$ birinchi tartibli reaksiya bo'lib, $T_1 = 323,2$ K da yarim ajralish vaqti 100 min, $T_2 = 353,2$ K da esa 15 min. Reaksiyaning harorat ko'effitsiyenti va tezlik konstantasini aniqlang.

56. Sirka kislota etil efiri $\text{CH}_3\text{COOC}_2\text{H}_5$ ning NaOH bilan sovunlash reaksiyasining tezlik konstantasi $T_1 = 282,2$ K da $k = 2,37$, 287,3 K da $k_2 = 3,204$ ga teng. Qaysi haroratda $k_3 = 4$ bo'ladi?

57. Eritmada 0,1 mol etilasetat va 0,1 mol NaOH bo'lganida 283,2 K da 15 minutda 10% efir sovunlangan. 298,2 K da esa shu vaqtda 20% efir sovunlangan. 313,2 K da 5 min davomida necha foiz efir sovunlanadi? Shu haroratda tezlik konstantasi qanchaga teng?

58. $T = 300$ K da harorat ko'effitsiyenti 3,5 ga teng. Aktivlanish energiyasini aniqlang.

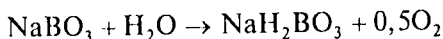
59. Uchxlor sirka kislota CCl_3COOH karbonsizlanish reaksiyasining aktivlanish energiyasi 180 kJ/mol ga teng, 300 K da harorat ko'effitsiyenti qanchaga teng bo'ladi?

60. Quyida keltirilgan ma'lumotlardan foydalanib, A moddaning ishqor ta'sirida gidrolizlanish reaksiyasining aktivlanish energiyasini toping. Grafik usuldan foydalaning.

T, K	298	303	307,5	312	321	330
$k \cdot 10^4, \text{sek}^{-1}$	0,40	0,75	0,93	1,48	3,03	7,72

61. 25°C va 35°C da olib borilganda reaksiyaning tezlik konstantalari: a) 2 marta, b) 3 marta, d) 5 marta, e) 10 marta oshgan. Reaksiyaning aktivlanish energiyasini toping.

62. Natriy perboratning ajralish reaksiyasi



birinchi tartibli reaksiya. Reaksiyaning tezlik konstantasi $T_1 = 303,2$ K da $k_1 = 2,2 \cdot 10^{-3} \text{ min}^{-1}$ ga, $T_2 = 308,2$ K da $k_2 = 4,1 \cdot 10^{-3} \text{ min}^{-1}$ ga teng. Reaksiyaning aktivlanish energiyasini aniqlang. $T_3 = 313,2$ K da va qancha vaqtdan so'ng perborat 99,99% gacha parchalanadi?

63. Izopropil efirning gaz holatda allilasetonga o'tish — izomerlanish reaksiyasi birinchi tartibli reaksiyadir. Tezlik konstantasining haroratga qarab o'zgarishi $k = 5,4 \cdot 10^{11} e^{-29300/RT}$ tenglamasi bilan ifodalanadi. Reaksiyada dastlab izopropil efirning bosimi $1,0133 \cdot 10^5 \text{ Pa}/760 \text{ mm}$ simob ustuniga teng bo'lgan. $T = 423,2$ K da izopropil efirning parsial bosimi qancha vaqtdan so'ng $4 \cdot 10^4 \text{ Pa}$ (300 mm simob ustuni) ga teng bo'ladi?

64. Ikkinchi tartibli reaksiyada $T_1 = 328,2$ va $T = 298,2$ K haroratda tezlik konstantalari mos ravishda $k_1 = 10^{-2}$ va 10^{-3} min^{-1} ga teng. Reaksiya uchun moddalar bir xil konsentratsiyada $C_A = C_B = 0,01 \text{ mol/l}$ olingan. $343,2$ K da tezlik qanchaga teng bo'ladi?

65. Katalizator reaksiyaning aktivlanish energiyasini 40 kJ/mol ga kamaytirgan. Reaksiya 300 K da olib borilgan. Katalizator reaksiya tezligini necha marta tezlatadi?

66. Katalizator reaksiyaning aktivlanish energiyasini 60 kJ/mol dan 20 kJ/mol gacha kamaytirgan. 300 K da katalizator qo'llash harorat koeffitsiyentini qanchaga kamaytiradi?

67. Katalizator mavjudligida aktivlanish energiyasi 8 kJ/mol ga kamaygan. 400 K da mahsulotning unumi (chiqishi) 25% bo'lgan. 500 K da unum qancha (%) bo'ladi?

68. A moddaning reaksiya tezligi $V = k(\Lambda)^3$ tenglamasi bilan ifodalanadi. $T_1 = 333,2$ K da $k_1 = 420 \cdot 10^{-6}$ ga, $T_2 = 473,2$ K da $k_2 = 1,4 \cdot 10^{-4}$ ga teng. Konsentrasiya simob ustunida ifodalanadi. Aktivlanish energiyasi, eksponensial oldidagi ko'paytuvchi (k)ni aniqlang.

69. Etilbromidning n propilbromidga pirolizi birinchi tartibli reaksiya. Turli haroratlarda pirolizning tezlik konstantalari quyidagi qiymatlarda teng bo'lgan:

T, K	800	833	877	900
k_1, sek^{-1}	0,0361	0,141	0,162	1,410
T, K	794	806	855	881
k_2, sek^{-1}	0,110	0,192	2,126	3,708

k_1 — etilbromidning pirolizlanish tezlik konstantasi; k_2 — ajralish reaksiyasining konstantasi. Grafik usulidan foydalanib, ikkala reaksiyaning aktivlanish energiyasi, eksponensial oldidagi kattalik (k_0) ni aniqlang. Analitik ko'rinishda tezlik konstantasining harorat bilan o'zgarishini ifodalang.

70. $2\text{HJ} \xrightleftharpoons[k_2]{k_1} \text{H}_2 + \text{J}_2$ reaksiyaning tezlik konstantasi 668,8 K

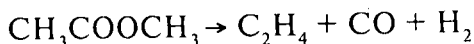
da $k = 0,259$, $k_2 = 15,59$ ga, 698,6 K da $k = 1,242$ va $k_2 = 67,0 \text{ sm}^3 \cdot \text{mol}^{-1} \cdot \text{sek}^{-1}$ ga teng:

a) to'g'ri va qaytar reaksiya tezlik konstantasining harorat bilan o'zgarishini; b) dissotsilanish muvozanat konstantasining harorat bilan o'zgarishini; d) 553 K va 703 K da muvozanat konstantasi qiymatlarini aniqlang.

71. Azot oksidning ajralish reaksiyasi $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ gaz fazada boradigan bimolekular reaksiya. 627 K da tezlik konstantasi $k = 1,81 \cdot 10^3 \text{ sm}^3 \cdot \text{mol}^{-1} \cdot \text{sek}^{-1}$. Sterik faktor $P = 0,019$.

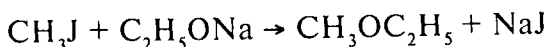
NO_2 molekulasining diametri $d = 3,55 \cdot 10^{-8} \text{ sm}$. Aktivlanish energiyasi (E) ni aniqlang.

72. Asetonning ajralish reaksiyasi



aktivlanish energiyasi $E = 286,6 \text{ kJ/mol}$. Aseton molekulasining diametri $d = 5,0 \cdot 10^{-8} \text{ sm}$. 835 K va 760 mm simob ustuni bosimida reaksiyaning tezlik konstantasini hisoblab toping.

73. 291 K da metil yodid bilan natriy etilat o'rtasidagi reaksiyaning



tezlik konstantasi $k = 4,96 \cdot 10^{-4} \text{ l} \cdot \text{mol}^{-1} \cdot \text{sek}^{-1}$ ga teng. Sterik faktor $P = 0,8$ molekular radiusi $Z_A = 2,64 \cdot 10^{-8} \text{ sm}$, $Z_B = 2,74 \cdot 10^{-8} \text{ sm}$. Reaksiyaning aktivlanish energiyasi (E) ni aniqlang.

74. Trietilamin (C_2H_5)₃N etilenbromid $\text{C}_2\text{H}_5\text{Br}$ bilan boruvchi reaksiyasi ikkinchi tartibli reaksiya bo'lib, bir tomonga boruvchi reaksiyada tezlik konstantasi harorat bilan quyidagicha o'zgaradi:

$T \text{ K}$	273,12	283,2	293,2	303,2
$k \cdot 10^3, \text{ sm}^3 \cdot \text{mol}^{-1} \cdot \text{sek}^{-1}$	0,28	0,558	1,17	2,22

Ularning zichligi mos ravishda $d_A = 0,723$ va $d_B = 1,456 \text{ g/sm}^3$ ga teng. Reaksiyaning aktivlanish energiyasi (E) va sterik faktor (P) ni aniqlang.

75. Dimetilbenzilaminning metil yodid nitrobenzol muhitda boradigan reaksiyasida tezlik konstantasi turli haroratlarda quyidagi qiymatlarga ega bo'ladi:

T K	273,2	283,2	293,2	303,2
$k \cdot 10^3, \text{sm}^3 \cdot \text{mol}^{-1} \cdot \text{sek.}^{-1}$	0,922	1,64	4,615	9,63

Ularning zichligi mos ravishda $d_A = 0,956$, $d_B = 2,28 \text{ g/sm}^3$.

Reaksiya ikkinchi tartibli. Aktivlanish energiyasi (E) ni va sterik faktor (P) ni toping.

76. A efirning ishqordagi gidroliz reaksiyasining tezlik konstantasi harorat bilan quyidagicha o'zgaradi:

$T^\circ\text{C}$	25	30	34,5	39	48	57
$k \cdot 10^3, \text{sek}^{-1}$	0,50	0,68	1,03	1,62	3,95	8,95

Standart aktivlanish entalpiyasini (ΔH°) va standart aktivlanish entropiyasini (ΔS°) aniqlang.

77. A moddaning kislotali muhitdagi gidroliz reaksiyasining tezlik konstantasi harorat bilan quyidagicha o'zgargan:

$T^\circ\text{C}$	15,54	25,00	34,55	44,92
$k, \text{min.}$	0,138	0,302	0,638	1,22

Standart aktivlanish entalpiyasi ΔH° va standart aktivlanish entropiyasi ΔS° qiymatlarini aniqlang.

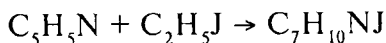
78. Reaksiyaning tezlik konstantasi 100 min^{-1} . Standart Gelmgols energiyasi ΔF° ni toping.

79. Birinchi tartibli ikkita reaksiyada aktivlanish energiyasi (E) ga teng. Lekin standart aktivlanish entropiya ΔS° si 42 J/mol ga farq qiladi. 300 K da ularning tezlik konstantalari nisbatini toping.

80. 673 K da etilenning dimerlanish reaksiyasi $2 \text{ C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_8$ tezlik konstantasi qiymatlarini aniqlang.

$$1 - \text{buten uchun } \Delta H^\circ = 147465 \text{ J/mol}, \Delta S^\circ = -147 \text{ J/mol} \cdot \text{grad}.$$

81. Piridin bilan etil yodid reaksiyasining



303 K da tezlik konstantasi $k = 1,72 \cdot 10^{-6} \text{ l/mol} \cdot \text{sek}$ ga teng. $\Delta S^* = -118,5 \text{ J/mol} \cdot \text{grad}$. ΔH^* va E — aktivlanish energiyaning qiymatlarini aniqlang.

82. Oltinugurt (IV) oksidining oksidlanish reaksiyasi tekshirilganda to'g'ri va teskari reaksiyasining tezlik konstantalari harorat o'zgarishi bilan quyidagi qiymatlarda bo'lgan:

$T \text{ K}$	873	879	898	933	938	947
k_1, min^{-1}	82,5	82,0	132,0	196,0	209,0	279
k_2, min^{-1}	9,95	11,8	23,8	52,3	58,25	85,60

To'g'ri va teskari reaksiyalar uchun ΔH^* va ΔS^* ning qiymatini toping.

83. Sulfamid kislota gidrolizlanish reaksiyasining 363 K da tezlik konstantasi $k = 1,16 \cdot 10^{-3} \text{ l/mol} \cdot \text{sek}$. Aktivlanish energiyasi $E = 127,49 \text{ kJ/mol}$. Reaksiya uchun ΔH^* va ΔS^* qiymatlarini toping.

84. $A \rightarrow B$ bizomerlanish reaksiyasi tezlik konstantasining haroratga bog'liq holda o'zgarishi quyidagicha:

$T^\circ\text{C}$	64,3	67,2	69,8	72,0	74,6
$k \cdot 10^4, \text{sek}^{-1}$	0,46	1,11	2,69	7,30	14,59

Reaksiyaning aktivlanish energiyasi (E), ΔH^* va ΔS^* qiymatlarini aniqlang.

86. Fosfonatning fosfatga aylanish reaksiyasi tezlik konstantasi haroratga bog'liq holda quyidagicha o'zgaradi:

$T^\circ\text{C}$	32,6	42,3	44,6	54,1	57,1
$k \cdot 10^4, \text{mol}^{-1} \cdot \text{sek}$	0,40	1,07	1,33	3,15	3,80

ΔH^* va ΔS^* ni aniqlang.

KO'P VARIANTLI MASALALAR

1. n - tartibli A reaksiya uchun har xil haroratda tezlik konstantasi qiymati berilgan.

Birinchi tartibli ($n = 1$) reaksiya uchun k ning o'lchami sek^{-1} , $n = 2$ reaksiyalar uchun sm^3/sek molda berilgan. Bu yerda:

- a) aktivlanish energiyasi E ni;
- b) eksponensial oldidagi kattalik (k_0)ni;
- d) aktivlanish issiqligi ΔH° ni;
- e) aktivlanish entropiyasi ΔS° ni;
- f) reaksiya tezligining harorat ko'effitsiyenti (γ)ni aniqlang.

Nº	A reaksiya	T K	k
1	2	3	4
1	$(\text{CH}_2)_6\text{C} \begin{cases} \text{Cl} \\ \text{Cl} \end{cases}$ ning 80% li etanidagi gidrolizi $n=1$	273 298 308 318	$1,00 \cdot 10^{-5}$ $3,19 \cdot 10^{-4}$ $9,86 \cdot 10^{-4}$ $2,92 \cdot 10^{-3}$
2	$\text{N}_2\text{O} \rightarrow \text{N}_2\text{O}_4 + 0,5\text{O}_2$ $n = 1$	273,1 288,1 293,1 298,1 313,1 318,1 323,1 328,1 338,1	$7,87 \cdot 10^{-7}$ $1,05 \cdot 10^{-5}$ $1,76 \cdot 10^{-5}$ $3,38 \cdot 10^{-5}$ $2,47 \cdot 10^{-4}$ $4,98 \cdot 10^{-4}$ $7,59 \cdot 10^{-4}$ $1,50 \cdot 10^{-3}$ $4,87 \cdot 10^{-3}$
3	Suv eritmasida asetodikarboksil kislotaning parchalanishi	273,2 293,2 333,2	$2,46 \cdot 10^{-5}$ $47,5 \cdot 10^{-5}$ $5480 \cdot 10^{-5}$
4	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + 0,5\text{O}_2$ $n = 1$	273,2 298,2 308,2 318,2 328,2 338,2	$7,67 \cdot 10^{-7}$ $3,46 \cdot 10^{-5}$ $1,40 \cdot 10^{-4}$ $4,98 \cdot 10^{-4}$ $1,50 \cdot 10^{-3}$ $4,87 \cdot 10^{-3}$
5	$\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$ $n = 1$	750 760 770 780 790 800	$4,539 \cdot 10^{-3}$ $7,194 \cdot 10^{-3}$ $1,25 \cdot 10^{-2}$ $1,741 \cdot 10^{-2}$ $2,667 \cdot 10^{-2}$ $4,140 \cdot 10^{-2}$

1	2	3	4
6	$\text{N}_2\text{O}_4 \rightarrow 2\text{N}_2\text{O}$ $n = 1$	300 310 320 330 340 350	$3,288 \cdot 10^6$ $6,652 \cdot 10^6$ $1,259 \cdot 10^7$ $2,398 \cdot 10^7$ $4,295 \cdot 10^7$ $7,447 \cdot 10^7$
7	Sikl (halqa) $(\text{CH}_3\text{CHO})_2 \rightarrow$ $2\text{CH}_3\text{CHO}$ $n = 2$	500 510 520 530 540 550	$5,175 \cdot 10^{-5}$ $1,238 \cdot 10^{-4}$ $2,345 \cdot 10^{-4}$ $6,455 \cdot 10^{-4}$ $1,404 \cdot 10^{-3}$ $2,994 \cdot 10^{-3}$
8	$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{HBr} \rightarrow$ $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ $n = 2$	300 310 320 330 340 350 360	$7,638 \cdot 10^{-7}$ $2,055 \cdot 10^{-6}$ $6,309 \cdot 10^{-6}$ $1,388 \cdot 10^{-5}$ $5,188 \cdot 10^{-4}$ $5,902 \cdot 10^{-4}$ $6,020 \cdot 10^{-3}$
9	$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$ $n = 2$	600 610 620 630 640 650 660	$7,413 \cdot 10^{-3}$ $1,343 \cdot 10^{-2}$ $2,38 \cdot 10^{-2}$ $4,149 \cdot 10^{-2}$ $7,145 \cdot 10^{-2}$ $7,586 \cdot 10^{-1}$ $1,995 \cdot 10^{-1}$
10	$\text{H}_2 + \text{J}_2 \rightarrow 2\text{HJ}$ $n = 2$	500 510 520 530 540 550 560	$7,834 \cdot 10^{-4}$ $1,714 \cdot 10^{-3}$ $92,43 \cdot 10^{-3}$ $7,48 \cdot 10^{-3}$ $1,503 \cdot 10^{-2}$ $2,930 \cdot 10^{-2}$ $5,610 \cdot 10^{-2}$
11	$\text{HJ} + \text{CH}_3\text{J} \rightarrow \text{CH}_4 + \text{J}_2$ $n = 2$	400 410 420 430 440 450 460	$9,954 \cdot 10^{-5}$ $2,780 \cdot 10^{-4}$ $7,396 \cdot 10^{-4}$ $1,884 \cdot 10^{-3}$ $4,592 \cdot 10^{-3}$ $5,370 \cdot 10^{-3}$ $2,427 \cdot 10^{-2}$

1	2	3	4
12	$2\text{HJ} \rightarrow \text{H}_2 + \text{J}_2$ $n = 2$	500 510 520 530 540 550 560	$2,938 \cdot 10^{-6}$ $7,096 \cdot 10^{-6}$ $1,652 \cdot 10^{-5}$ $1,732 \cdot 10^{-5}$ $8,143 \cdot 10^{-5}$ $1,742 \cdot 10^{-4}$ $3,606 \cdot 10^{-4}$
13	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ $n = 2$	350 360 370 380 390 400 410	$1,119 \cdot 10^{-4}$ $4,130 \cdot 10^{-4}$ $1,119 \cdot 10^{-3}$ $2,222 \cdot 10^{-3}$ $7,499 \cdot 10^{-3}$ $1,786 \cdot 10^{-2}$ $4,083 \cdot 10^{-2}$
14	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} =$ $= \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$	250 290 300 310 320 330	24,378 48,865 93,540 122,460 216,272 360,828
15	$\text{CH}_3\text{Br} + \text{NaJ} \rightarrow \text{CH}_3\text{J} + \text{NaBr}$	280 290 300 310 320 330	$8,395 \cdot 10^{-2}$ $2,075 \cdot 10^{-1}$ $7,55 \cdot 10^{-1}$ 2,032 5,152 12,33
16	$2\text{H}_2\text{C} = \text{HC} - \text{HC} = \text{CH}_2 \rightarrow$ $\rightarrow \text{CH}_2 = \text{C} \begin{cases} \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\ \text{CH}_2 - \text{CH} = \text{CH}_4 \end{cases}$	503 513 513 517 530 540 555 578 606 622 642	0,531 0,751 1,19 1,40 1,70 2,43 4,18 9,85 25,4 44,5 84,4
17	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $n = 2$	973 1023 1073 1221 1273 1323	$0,14 \cdot 10^{-3}$ $0,28 \cdot 10^{-4}$ $0,14 \cdot 10^{-3}$ 0,012 0,018 0,024

XI.6. ZANJIR REAKSIYALAR

Zanjir mexanizmi bilan boradigan reaksiyalarning boshlanishi va reaksiya davom etishi uchun, eng avvalo, aktiv markazlar mavjud bo'lishi kerak. Aktiv markazlar **ozod radikal** (radikal)lar, ya'ni tashqi elektron qatlamida juftlanmagan yakka elektronga (ya'ni ozod valentlikka) ega bo'lgan atom va molekulalardir. Radikallar modda simvoli ustiga nuqta qo'yib tasvirlanadi ($H^\cdot$, $OH^\cdot$, $Cl^\cdot$) va hokazo.

Ozod radikallar nur, γ nurlanish, β yoki α zarrachalar va boshqa initsiatorlar ta'sirida hosil bo'lishi mumkin. Ozod radikal (initsiatorning parchalanishi natijasida hosil bo'lgan radikal)lar monomer modda bilan reaksiyaga kirishib, uni aktiv markazga aylantiradi. Initsiator sifatida o'zgaruvchan valentli metallar, benzol peroksidi va boshqa organik peroksidlar bo'lishi mumkin.

Dastlabki moddalardan mahsulotlarning hosil bo'lishi, ozod valentlik (yakka elektronli) saqlangan holda, ozod radikallar ishtirokida muntazam ravishda birin-ketin boradigan reaksiyalar natijasida sodir bo'ladigan jarayonga **zanjir reaksiyalar** deyiladi. Zanjir reaksiyalar uch asosiy bosqichni o'z ichiga oladi:

a) aktiv markazlarning hosil bo'lishi — **zanjirning paydo bo'lishi** — zanjir reaksiyasi aktiv markazlari (radikal atomlar)ning hosil bo'lishi;

b) **zanjirning uzilishi** — aktiv markazlarning yo'qolish reaksiyasi;

d) **zanjirning davom etishi** — tarmoqlanmasdan va tarmoqlanib davom etishi.

Zanjirning paydo bo'lish reaksiyasida har qaysi molekuladan 2 ta ozod radikal hosil bo'lsa, reaksiya tezligi(v_0):

$$v_0 = 2k_0[J], \quad (XI. 50)$$

k_0 — initsiatorning ozod radikallarga aylanish reaksiyasining tezlik konstantasi; $[J]$ — initsiator (ozod radikal hosil qiluvchi molekula) konsentratsiyasi.

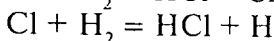
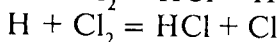
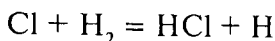
Agar 1 molekula initsiator parchalanganida ikkita radikal hosil bo'lsa, zanjirning paydo bo'lish tezligi

$$v_0 = 2 \frac{d[I]}{dt} = 2K_0[I]$$

ga teng bo'ladi.

Tarmoqlanmagan zanjir reaksiyalar

Tarmoqlanmagan zanjir reaksiyalarda zanjirning har qaysi bosqichida yo'qolgan **bitta** aktiv markaz o'rniga **bitta** yangi aktiv markaz hosil bo'ladi. Masalan, $H_2 + Cl_2 = 2HCl$ reaksiyasida:



va hokazo.

Zanjirning uzilishi ikki joyda sodir bo'lishi mumkin: idish devorlarida — birinchi darajali uzilish va idish ichida — ikkinchi darajali uzilish.

Agar uzilish birinchi darajali bo'lsa va faqat bitta radikal yo'qolib, zanjirda uzilish sodir bo'lsa, bu reaksiya tezligi

$$v_0 = k_3[\dot{R}_1]. \quad (XI.51)$$

Agar uzilish ikkinchi darajali bo'lsa:

$$v_0 = 2k_3[\dot{R}_1]^2. \quad (XI.52)$$

Bu tenglamada v_0 — aktiv markaz (radikallarning) yo'qolish reaksiyasi tezligi, $[\dot{R}_1]$ — yo'qolgan radikal konsentratsiyasi, K_3 — zanjirning uzilish reaksiyasi tezligi. Yuqoridagi tenglamadan ozod radikalning konsentratsiyasi birinchi darajali uzilishda $[\dot{R}_1] = v_0/k_3$ ga, ikkinchi darajali uzilishda $[\dot{R}_1] = \sqrt{v_0/2k_3}$ ga teng. Demak, zanjir reaksiyasining tezligi (v):

birinchi darajali uzilishda:

$$v = k_i \frac{v_0}{k_3} [A_i], \quad (\text{XI.53})$$

ikkinchi darajali uzilishda:

$$v = k_i \sqrt{v_0 / 2k_3} [A_i]. \quad (\text{XI.54})$$

A_i — dastlabki moddalar.

Ozod radikallar ishtirokida zanjirning davom etishida asosan zanjir uzilishi sodir bo'lgan bosqich zanjirning tezligini chegaralovchi (belgilovchi) bosqich bo'ldi.

i — zanjir reaksiyani belgilovchi (chegaralovchi bosqich) reaksiyaga mansub.

Agar belgilovchi (limitlovchi) bosqich monomolekular bo'lsa, zanjir reaksiyaning tezligi birinchi darajali uzilishda:

$$v = k_i \frac{v_0}{k_3}, \quad (\text{XI.55})$$

ikkinchi darajali uzilishda:

$$v = k_i \sqrt{v_0 / 2k_3} \quad (\text{XI.56})$$

ga teng bo'ladi.

Zanjir uzunligi — bosqichlar soni (t) zanjir reaksiya tezligining zanjirning uzilishi tezligiga yoki zanjirning hosil bo'lish tezligi nisbatiga teng:

$$v = \frac{V}{V_{uzilish}} = \frac{V}{V_0}. \quad (\text{XI.57})$$

Shunga ko'ra birinchi darajali uzilishda zanjir uzunligi (v):

$$v = (k_1 / k_3) [A_i], \quad (\text{XI.57}^1)$$

ikkinchi darajali uzilishda:

$$v = \frac{ki}{\sqrt{2k_3V_0}}. \quad (XI.58)$$

Shunday birinchi darajali uzilishda zanjir uzunligi zanjirning hosil bo'lish tezligiga bog'liq emas. Ikkinchi darajali uzilishda esa zanjir uzunligi zanjirning hosil bo'lish reaksiya tezligi darajali ildiziga teskari proporsionaldir.

Zanjir hosil bo'lishi, uning uzilishi va zanjirning davom etishi reaksiyalarining tezlik konstantalari *foydali tezlik konstantasi* deyiladi. Effektiv tezlik konstantasining harorat bilan o'zgarishi Arrenius tenglamasi bilan ifodalanadi va bunda aktivlanish energiyasi birinchi darajali uzilishda:

$$E_{ef} = E_0 + E_1 - E_3, \quad (XI.59)$$

E_0 — zanjir hosil bo'lish reaksiyasiga,

E_1 — zanjirning davom etish reaksiyasiga,

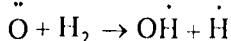
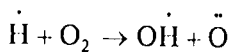
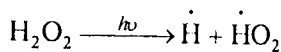
E_3 — zanjirning uzilish reaksiyasiga mansub.

Ikkinchi darajali uzilishda:

$$E_{ef} = \frac{1}{2} E_0 + E_1 - E_3. \quad (XI.60)$$

Tarmoqlangan zanjir reaksiyalar

Tarmoqlangan zanjir reaksiyada har qaysi bosqichda reaksiyaga kirishib yo'qolgan bitta aktiv markaz o'rnida birdan ortiq aktiv markaz hosil bo'ladi. Masalan, $H_2 + O_2 = 2H_2O$ reaksiyalarda:



Birinchi darajali zanjir uzilishda aktiv markaz uchun kinetik tenglama quyidagicha bo'ladi:

$$\frac{dn}{dt} = V_0 + f_n - g_n. \quad (XI.61)$$

Agar $\varphi = f - g$ deb belgilasak:

$$\frac{dn}{dt} = V_0 + \varphi_n. \quad (\text{XI.62})$$

Bunda: n — ozod radikallar yig'indisi; v_0 — zanjirning hosil bo'lish tezligi; g — birinchi darajali uzilishning tezlik konstantasi; f — reaksiya boshlanishida dastlabki moddalarning reaksiyaga kirishgan miqdorini e'tiborga olmagandagi ko'paytiruvchi bo'lib, uni turg'un miqdor desa ham bo'ladi.

Agar $f < g$, ya'ni $4 < 0$ bo'lsa, bu tenglama integrallanganda quyidagi tenglama olinadi:

$$n = \frac{V_0}{\varphi} = (1 - e^{\varphi t}). \quad (\text{XI.63})$$

Bu tenglama aktiv markazlarning vaqt o'tishi bilan to'planishini ifoda etadi. Bu tenglamaga muvofiq ma'lum vaqtdan so'ng sistemada statsionar, ya'ni aktiv markazlarning o'zgarmas konsentratsiyasi qaror topadi:

$$n = \frac{V_0}{\varphi} = \frac{V_0}{f - g}. \quad (\text{XI.64})$$

Bunda zanjirning tarmoqlanishi faqat aktiv molekulalarning statsionar konsentratsiyasini orttiradi, $f = 0$ bo'lganga nisbatan zanjir uzilish tezligi biroz kamayadi.

Agar $f > g$, ya'ni $f > 0$ bo'lib, yuqoridagi tenglama integrallansa, quyidagi tenglama olinadi:

$$n = \frac{V_0}{\varphi} = (e^{\varphi t} - 1). \quad (\text{XI.65})$$

Ma'lum vaqtdan so'ng φ 1 dan katta bo'lganda:

$$n = \frac{V_0}{\varphi} e^{\varphi t}. \quad (\text{XI.66})$$

Bu holda aktiv markaz konsentratsiyasi muntazam ravishda ortadi va natijada reaksiya tezligi ham eksponensial tarzda orta borib, nihoyat reaksiya portlash bilan tugaydi.

XI.7. FOTOKIMYOVIIY REAKSIYALAR

n molekula ma'lum qalinlikdagi eritmadan nur oqimi o'tkazilganda nur intensivligi Lambert-Ber qonuniga binoan quyidagicha o'zgaradi:

$$I = I_0 e^{-knE}, \quad (XI.67)$$

bunda: I — eritmadan o'tgan nur oqimi intensivligi; I_0 — nur oqimining eritmadan o'tishidan oldingi intensivligi; n — nur yutuvchi molekulalarning 1 sm^3 hajmdagi miqdori; k — nur yutilishining molekular koeffitsiyenti.

Muhit (eritmaning) energiyani yutishini Vant-Goff qonuni ifoda qiladi:

$$E = J_0(1 - e^{-knl}). \quad (XI.68)$$

E — vaqt birligida yutilgan energiya.

Fotokimyoviy reaksiyalarning miqdoriy ifodasi reaksiya unumi (γ) bilan tavsiflanadi. γ — 1 kvant energiya yutilganda qancha reaksiya sodir bo'lganini (reaksiya kvant unimini) ko'rsatadi:

$$\gamma = \frac{n_1}{n_2}, \quad (XI.69)$$

n_1 — 1 sm^3 hajmda va 1 sek da 1 kvant nur yutilganda reaksiyaga kirishgan molekulalar soni; n_2 — hajm birligida (sm^3) va 1 sek da yutilgan kvantlar soni.

$$n_2 = E/h\nu.$$

Fotokimyoviy reaksiyalarning kinetik tenglamasi quyidagicha bo'ladi:

$$-\frac{dn}{dt} = \gamma I_0(1 - e^{-knl}). \quad (XI.70)$$

$\gamma < 1$, ya'ni γ — 1 ga teng yoki 1 kichik bo'ladi. Lekin ba'zan 1 dan katta ham bo'ladi. Bunga sabab nurning yutilishida zanjirning aktiv markazlarining hosil bo'lishi, natijada fotokimyoviy reaksiya bilan bir qatorda zanjir reaksiyaning borishidir.

MASALALAR YECHISHGA DOIR MISOLLAR

1. Quyidagi ma'lumotlardan foydalanib, uroniloksalatning ajralish reaksiyasi unumini har qaysi to'qlin uchun hisoblang.

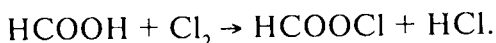
№	To'qlin uzunligi, nm	Oksalatning ajralgan molar qismi	Ajralgan molekular soni, 10^{-18}	Yutilgan fotonlar soni, 10^{-18}
1	365,5...	0,0592...	5,18...	10,58
2	365,5...	0,0498...	4,32...	8,93
3	435,8...	0,0242...	2,10...	3,64
4	435,8...	0,0208...	1,79...	3,10

Y e c h i s h . (XI.69) tenglamadan foydalanib 365,5 to'qlin uchun.

$$\gamma = \frac{\text{ajralgan molekular soni}}{\text{yutilgan fotonlar soni}} = \frac{5,10^{18}}{10,58 \cdot 10^{18}} = 0,490 .$$

Qolgan to'qlinlar uzunliklari uchun: $\gamma = 0,490$; $0,483$; $0,576$; $0,577$.

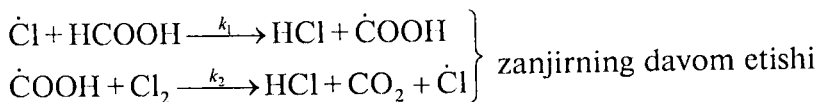
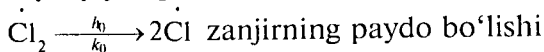
2. Chumoli kislotani xlorlash reaksiyasi gaz fazada nur ta'sirida zanjir mexanizmi bo'yicha boradi:



Bu reaksiyaning tezligi tajribada olingan natijalarga muvofiq quyidagicha tenglama bilan ifodalanadi:

$$\frac{d[\text{Cl}]}{dt} = k[\text{Cl}_2][\text{ClCOOH}].$$

Reaksiyaning tezlik konstantasi (k) ifodasini keltiring. Zanjir reaksiya quyidagi sxema bo'yicha boradi:



$\dot{\text{Cl}} + \text{devor} \xrightarrow{k_3} \text{Cl}$, bunda Cl idish devoriga adsorбилangan, ya'ni zanjirning uzilishi sodir bo'ladi.

Y e c h i s h . Zanjir uzilishi birinchi darajali bo'lganida reaksiya tezligi (XI.53) tenglama bilan ifodalanadi:

$$V = k_i \frac{V_0}{k_3} [\text{Ai}].$$

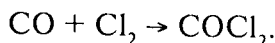
Zanjirning uzilishi Cl atomida sodir bo'lganida $k_2 = k_1$ va bu qiymatlar yuqoridagi tenglamaga qo'yilsa:

$$V = \frac{k_1 k_0}{k_3} [\text{Cl}_2] [\text{HCOOH}].$$

Agar bu tenglama tajribada topilgan tenglama bilan solishtirilsa:

$$k = \frac{k_1 k_0}{k_3}.$$

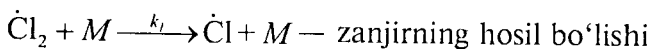
3. Fosgenning hosil bo'lish reaksiyasi:

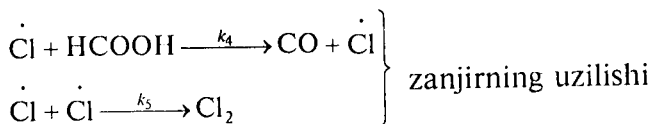
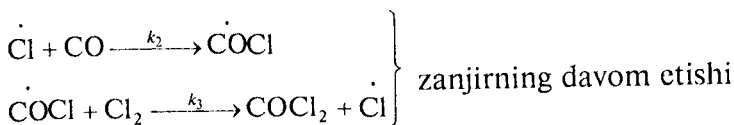


Nur ta'sirida reaksiya zanjir mexanizmi bo'yicha boradi. Tajribada bu reaksiya tezligi quyidagi tenglama bilan borishi aniqlangan:

$$\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2].$$

Reaksiya quyidagi bosqichlarda boradi (M — idish devori):





Reaksiya tezligi ifodasini keltirib chiqaring.

Y e c h i s h . Uzilish Cl atomida boradi. Statsionar (o'zgarmas) holatda zanjirning Cl bo'yicha hosil bo'lishi va uzilish tezligi teng bo'ladi:

$$k_1[\text{Cl}_2][M] = k_3[\text{Cl}]_2 + M,$$

bundan:

$$[\text{Cl}] = \sqrt{\frac{k_1}{k_3}}[\text{Cl}_2].$$

COCl reaksiya uchun ham shunday bo'ladi:

$$k_2[\text{CO}][\dot{\text{Cl}}] = k_3[\dot{\text{COCl}}][\text{Cl}_2] + k_4[\text{COCl}]\dot{\text{CO}}$$

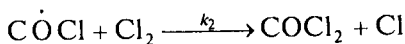
va

$$[\dot{\text{COCl}}] = \frac{k_2[\text{CO}][\text{Cl}]}{k_3[\text{Cl}_2] + k_4}.$$

Agar bu tenglamaga ($\dot{\text{Cl}}$) qiymati qo'yilsa, tezlikni dastlabki moddalar konsentratsiyasi orqali ifoda qilish mumkin:

$$[\dot{\text{COCl}}] = \frac{k_2[\text{CO}] \sqrt{\frac{k_1}{k_3}}[\text{Cl}_2]^{3/2}}{k_3[\text{Cl}_2] + k_4}$$

$[\dot{\text{COCl}}]$ ning bu qiymatiga COCl_2 ning hosil bo'lish tenglamasi qo'yilsa:



hosil bo'lish tezligi:

$$\frac{d[\text{COCl}_2]}{dt} = k_3[\dot{\text{C}}\text{OCl}][\text{Cl}_2].$$

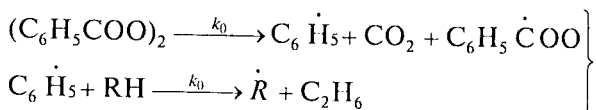
Bu tenglamaga $[\dot{\text{C}}\text{OCl}]$ ning yuqoridagi qiymati qo'yilsa:

$$\frac{d[\text{COCl}_2]}{dt} = \frac{k_1 k_3 [\text{CO}] \sqrt{\frac{k_1}{k_2} [\text{Cl}]^3}}{k_3 [\text{Cl}_2] + k_4}$$

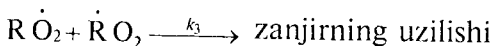
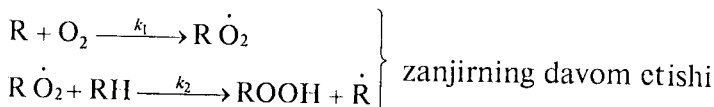
$$\frac{d[\text{COCl}_2]}{dt} = \frac{k_2 k_3 \left(\frac{k_1}{k_2}\right)^{\frac{1}{2}} [\text{CO}] [\text{Cl}_2]^{\frac{3}{2}}}{k_2 [\text{Cl}_2] + k_4}$$

Agar $k_4 \gg k_3 (k_2)$ bo'lsa, tajribada olingan yuqoridagi tenglama chiqadi. Haqiqatan ham, $\text{COCl} \xrightarrow{k_4} \text{CO} + \text{Cl}$ reaksiyasi juda kichik aktivlanish energiyasini talab qiladi va katta aktivlanish energiyasini talab qiladigan $\text{Cl} + \text{Cl} + \text{N} \xrightarrow{k_5} \text{Cl}_2 + \text{N}$ reaksiyaga nisbatan ancha tez boradi.

4. Uglevodorod benzoil peroksidi (initsiator) ishtirokida va nur ta'sirida kislorod molekulasini bilan suyuq fazada oksidlangan. Jarayon quyidagi bosqichlarda boradi:



Initsiatorning parchalanishi va demak, zanjirning paydo bo'lishi



Reaksiyaning aktivlanish energiyasi 28,5 kJ, reaksiya tezligi $v = 9,5 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1} \cdot \text{sek}^{-1}$. Zanjirning hosil bo'lish tezligi $v_0 = 9 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1} \cdot \text{sek}^{-1}$ ga teng. Initsiator ishtirokida reaksiyaning aktivlanish energiyasi 93,6 kJ ga teng. Initsiator benzoil peroksidi ajralish reaksiyasining aktivlanish energiyasi 128,9 J ga

teng. Zanjir uzunligi va har qaysi bosqichning aktivlanish energiyasi qanchaga tengligi aniqlansin.

Yechish. (XI.57) tenglamaga muvofiq zanjir uzunligi (ν):

$$\nu = \frac{V}{k_{uzilish}} = \frac{V}{V_0} = \frac{9,5 \cdot 10^{-6}}{9 \cdot 10^{-8}} = 105.$$

Reaksiyaning aktivlanish energiyasi zanjirning uzilishi ikkinchi darajada bo'lganida (XI.60) tenglamaga muvofiq:

$$E = \frac{1}{2} E_0 + E_1 - E_3,$$

E_0 — zanjirning hosil bo'lish bosqichiga, E_1 — zanjirning davom etish bosqichiga, E_3 — zanjirning uzilish bosqichiga tegishlidir.

Initsiatorning ajralishi zanjir reaksiyasining birinchi bosqichi bo'lib, nol energiyaning aktivlanish bilan bixilligidan

$$E = E_1 + \frac{1}{2} E_3 - 28,5 \text{ kJ} = 28,5 \text{ kJ}$$

va

$$E_1 - 0,5 E_3 = E - 0,5 E = 93,6 - 0,5 \cdot 128,9 \text{ kJ} = 28,9 \text{ kJ}.$$

Zanjirning uzilishi, ya'ni radikallarning yo'qolishi nolga yaqin aktivlanish energiyasi bilan borganligidan

$$E_1 - 0,5 E_3 = E_1 \text{ ga teng.}$$

MASALALAR

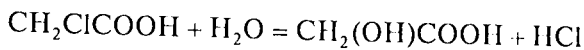
87. Xlorning benzildagi eritmasidan 35 minut davomida $\lambda=313$ nm to'liqindagi nur yuborilgan. Reaksiya natijasida $C_6H_6Cl_2$ moddasi hosil bo'lgan. Toza benzildan o'tgan energiya 46,81 J ga, eritmada reaksiya vaqtida o'tgan energiya 4,25 J ga teng bo'lgan. Natijada 1,8 g $C_6H_6Cl_2$ olingan. Kvant unumini toping.

88. $CO + Cl_2 \rightarrow COCl_2$ reaksiyasi borayotgan muhitga $\lambda = 400$ nm to'liqindagi nur yuborilgan va $3 \cdot 10^3$ J energiya yutilgan. Natijada 100 g fosgen hosil bo'lgan. Kvant unumini toping.

89. $3O_2 \rightarrow 2O_3$ reaksiyasida kvant unumi $\gamma = 3$ bo'lganda 1 mol ozon olish uchun to'liq uzunligi $\lambda = 207$ nm bo'lgan nurdan kislorod qancha energiya yutishi kerak?

90. Aseton $(CH_3)_2CO$ termik parchalanib, 578 K da uning 25% i 909 sek. da reaksiyaga kirishadi, 601 K da esa 25% miqdori 31 sek. da reaksiyaga kirishadi. Fotokimyoviy ajralish 313 nm uzunligidagi nurda kvant unumi $\gamma = 2$ da sodir bo'lgan. Monomolekular reaksiya bo'yicha boradigan termik parchalanishning tezlik konstantasini, aktivlanish energiyasini hisoblang. Shu natijaga erishish uchun fotokimyoviy jarayonda qancha energiya zarurligi (sarflanishi) ni aniqlang.

91. Monoxlorsirka kislotaning gidrolizi:

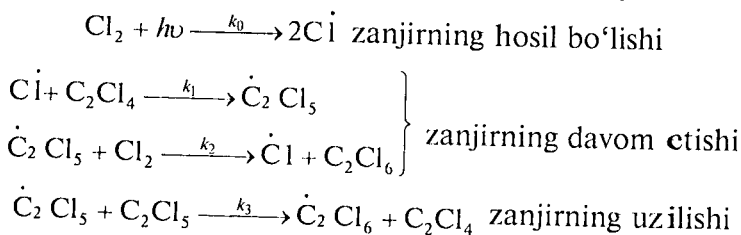


reaksiyasining tezlik konstantasi 353 K da $k = 2,22 \cdot 10^{-5}$ va 403 K da $k_2 = 2,37 \cdot 10^{-3} \text{ sek}^{-1}$ ga teng. Reaksiyaning aktivlanish energiyasi (E) ni toping. Fotokimyoviy jarayonda $k_1 = 2$ teng bo'lganda, $\lambda = 253,7$ nm nur o'tkazilganda qancha elektromagnit energiya yutiladi?

92. Tetraxlor etilenning fotokimyoviy xlorlanish reaksiyasi kinetikasi quyidagi tenglama bilan ifodalanadi:

$$\frac{dC_2Cl_4}{dt} = k[Cl_2]^{3/2}.$$

Bu zanjirli reaksiya bo'lib, u quyidagi sxema bo'yicha boradi:

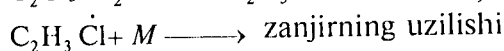
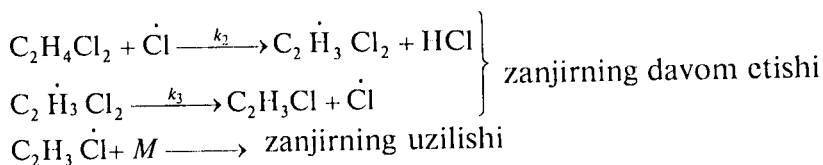
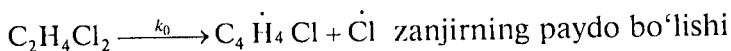


Yuqorida keltirilgan differensial tenglamani keltirib chiqaring.

93. Dixloretnaning gaz fazada termik ajralish reaksiyasi birinchi tartibli bo'lib, quyidagi differensial tenglama bilan ifodalanadi:

$$-\frac{d[\text{C}_2\text{H}_4\text{Cl}_2]}{dt} = k[\text{C}_2\text{H}_4\text{Cl}_2].$$

Reaksiya quyidagi sxema bo'yicha boradi:



Yuqorida keltirilgan differensial tenglamani keltirib chiqaring.

94. Butanning oksidlanishi tarmoqlangan zanjir reaksiyadir. Zanjir paydo bo'lish reaksiyasining aktivlanish energiyasi qiymatini toping. 100 sek. dan so'ng quyidagi natijalar olingan:

T, K	540	543	553
k, sek^{-1}	$2,5 \cdot 10^{-2}$	$9,3 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$
$n, \text{sm}^3 \cdot \text{sek}^{-1}$	$2,16 \cdot 10^9$	$1,98 \cdot 10^9$	$1,86 \cdot 10^9$

95. $\text{Br}_2 + \text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_{11}\text{Br} + \text{HBr}$ reaksiyasiga to'liq uzunligi $\lambda = 400 \text{ nm}$ nur berilganda 1 mol Br_2 reaksiyaga kirishgan. Kvant unumi $\gamma = 1$. Aralashmaga qancha nur energiyasi berilgan?

KO'P VARIANTLI MASALALAR

$A_1 + A_2 \rightarrow B_1 + B_2$ reaksiyasi tarmoqlangan zanjirli mexanizm bilan boradi. Zanjir paydo bo'lish reaksiyasi moddalardan birontasiga nur kvanti ta'sir qilishi yoki issiqlik (qizdirish) natijasida

sodir bo'ladi. Zanjirning davom etishi bosqich bilan boradi, deb faraz qilinadi. Zanjirning uzilishi jarayonda ishtirok etayotgan ozod radikallarning bittasida sodir bo'ladi. Quyidagilarni yozib ko'rsating:

1) zanjir reaksiyaning mo'ljallangan mexanizmi; 2) zanjir reaksiya uzunligidan foydalangan holda stexiometrik reaksiya; 3) zanjirning davom etish mexanizmi asosida zanjir uzilishi yuz bergan ozod radikalning tabiatiga qarab reaksiyaning kinetik tenglamasi turlicha bo'lishligini ko'rsating; 4) agar zanjir reaksiyaning uzunligi V bo'lsa, qancha miqdorda A_1 reaksiyaga kirishadi va qanchaga B_1 molekula hosil bo'ladi?

XII bob

KATALIZ

XII.1. GOMOGEN KATALIZ. KISLOTA-ASOS KATALIZI

Kislota va asoslar, aniqrog'i, vodorod ion H_3O^+ va OH^- gidroksil ionlar ko'pgina reaksiyalarni tezlatadi. Ularning reaksiyalarni tezlatish qobiliyati suyultirilgan, kuchsiz va kuchli asoslar uchun pHga bog'liq, konsentrlangan va kuchli kislotalar uchun Xammet funksiyasi H_0 ga bog'liqdir (H_0 — kislota ning reaksiyada proton berish qobiliyatini ko'rsatadi). Tezlik konstantasining qiymati kislota-asosning turiga qarab emas, balki pH, H_0 qiymatiga qarab o'zgaradi. Turli konsentratsiyada bir xil pH va H_0 ga ega bo'lgan kislota-asoslarning katalitik kuchi bir xil bo'ladi.

Ikkilamchi tuz effekti — kislota eritmasiga shu kislota ning tuzi qo'shilganda va birlamchi tuz effekti — kislota ga shu kislota ning ionlarini tutmagan tuz qo'shilganda ularning katalitik xossalari ning kuchayishi — H_3O^+ , OH^- bilan bir qatorda neytral molekullarning katalizator bo'lishini va katalitik sohaning ion kuchiga bog'liq ekanligini ko'rsatadi. Bu bog'lanishlar quyidagi tenglamalar bilan ifodalanadi:

$$\lg k = B - pH; \lg k = B - H_0, \ln k = \ln k_0 - 2AZ^+, Z \sqrt{I}, \quad (XII.1)$$

B — turg'un kattalik, k_0 — eritma cheksiz suyultirilgandagi konstanta, A — doimiy kattalik bo'lib, suv uchun 0,509 ga teng, Z^+ , Z^- — kation va anionlarning zaryad miqdori (valentligi), H_0 — turli kislotalarning turlicha konsentratsiyadagi qiymati ma'lumotnomalarda berilgan.

Kuchli kislotalar eritmasida reaksiya asosan gidroksoniy ioni H_3O^+ tomonidan tezlatiladi. Reaksiya tezligi:

$$V = k_{H_3O} + [H_3O^+][A]^{30+}; V = k_{H_3O} + C_{H_3O} + C_A, \quad (XII.2)$$

$[A]$ — reagent konsentratsiyasi.

№	Reaksiyalar	Nur kvanti yoki termik ta'sirga uchraydigan modda	Zanjir uzunligi, ν	Zanjir uzilishi sodir bo'lgan ozod radikal	Parchalana-digan molekula	Hosil bo'ladigan molekula	T K
1	$\text{Cl}_2 + \text{HCOOH} \xrightarrow{h\nu} \text{HCl} + \text{CO}_2$	Cl_2	30	Cl	HCOOH	HCl	298
2	$\text{C}_2\text{Cl}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6$	Cl_2	45	C_2H_5	Cl_2	C_2Cl_6	298
3	$\text{C}_2\text{H}_4\text{Cl}_2 \rightarrow$ termik parchalanish	$\text{C}_2\text{H}_4\text{Cl}_2$	50	$\text{C}_2\text{H}_3\text{Cl}_2$	$\text{C}_2\text{H}_4\text{Cl}_2$	HCl	298
4	$\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$ termik parchalanish	Cl_2	35	Cl_3	Cl_2	HCl	300
5	$\text{Cl}_2 + \text{H}_2 \xrightarrow{h\nu} 2\text{HCl}$	Cl_2	45	H_2	H_2	HCl	300
6	$\text{Br}_2 + \text{C}_6\text{H}_5\text{CH}_2 \xrightarrow{h\nu} \text{C}_6\text{H}_5\text{CH}_2\text{C}_2\text{H}_5$	Br_2	20	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_3$	HBr	300
7	$\text{CO} + \text{Cl}_2 \xrightarrow{h\nu} \text{COCl}_2$	Cl_2	500	Cl	Cl_2	COCl_2	300
8	$\text{CO} + \text{Cl}_2 \xrightarrow{h\nu} \text{COCl}_2$	Cl_2	300	Cl	CO	COCl_3	300
9	Metan CH_3 parchalanishi	CH_4	100	H	C_2H_4	C_2H_6	1000
10	Metan CH_3 parchalanishi	CH_4	80	CH_3	CH_4	H_2	1000
11	$\text{H}_2 + \text{Br}_2 \xrightarrow{h\nu} 2\text{HBr}$	Br_2	70	Br	Br_2	HBr	300
12	$\text{H}_2 + \text{Br}_2 \xrightarrow{h\nu} 2\text{HBr}$	Br_2	50	H	H_2	HBr	300
13	$2\text{O}_3 \xrightarrow{h\nu} 3\text{O}_2$	O_3	10	O	O_3	O_2	87
14	Termik parchalanish $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3\text{COCH}_3$	CH_3COCH_3	30	CH_3COCH_3	CH_3COCH_3	CH_4	500
15	Termik parchalanish $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CO} + \text{CH}_2$	CH_3COCH_3	50	CH_3	CH_3OCH_3	CH_4	500

Kuchli ishqoriy muhitda reaksiyani asosan gidroksil ioni OH^- tezlatadi. Reaksiya tezligi:

$$V = k_{\text{OH}} \cdot [\text{OH}^-][A]; \quad V = k_{\text{OH}^-} \cdot C_{\text{OH}^-} \cdot C_A. \quad (\text{XII. 3})$$

Agar reaksiya bir vaqtning o'zida vodorod va gidroksil ionlari ta'sirida tezlashsa:

$$k = k_0 + k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{\text{OH}^-}[\text{OH}^-], \quad (\text{XII. 4})$$

k_0 — katalizator bo'lmagan holatdagi tezlik.

Suvli eritmada:

$$k = k_0 + k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]. \quad (\text{XII. 5})$$

Reagentning ionlashgan C_{AH^+} konsentratsiyasi reagentning umumiy konsentratsiyasi (C_A) bilan quyidagicha bog'langan.

$$C_{\text{AH}^+} = \alpha C_A, \quad (\text{XII. 6})$$

α — dissotsilanish darajasi.

Demak, (XI.2) tenglamadan:

$$V = k C_{\text{AH}^+} = k \alpha C_A = k_{\text{ef}} C_A \quad (\text{XII. 7})$$

$$k_{\text{ef}} = \alpha k \text{ teng bo'ladi.} \quad (\text{XII. 8})$$

Katalizator mavjudligidagi reaksiyaning tezlik konstantasi **katalitik tezlik konstantasi** deb ham ataladi.

$\text{A} + \text{H}^+ \rightarrow \text{AH}^+$ tenglama uchun dissotsilanish muvozanat konstantasi (K_a):

$$K_a = \frac{C_{\text{AH}^+}}{C_A \cdot C_{\text{H}^+}}. \quad (\text{XII. 9})$$

Bu tenglamadan (AH^+) qiymati yuqoridagi tenglamalarga (XII. 3 va XII. 8) qo'yilsa:

$$K_{\text{ef}} = K - \frac{k_{\text{ef}} \cdot C_{\text{H}^+}}{k_a} \quad (\text{XII. 10})$$

yoki

$$\lg K_{\text{ef}} = \lg K - pK_a + \text{pH} \quad (\text{XII. 11})$$

$$(pK_a = -\lg K_a). \quad (\text{XII. 12})$$

Tajribada olingan natijalar koordinatalarga qo'yilsa, to'g'ri chiziq olinadi: chiziqning ordinata o'qi bilan kesishgan nuqtasi $1/K$ absissa o'qi bilan kesishgan nuqtasi K_a ga teng bo'ladi.

Bir xil kislota katalizida C_{HA} , α koeffitsiyentlar bir xil qiymatli (odatda kichik) bo'ladi.

Kislotali katalitik reaksiyalarda tezlik konstantasi k ning dissotsilanish konstantasi K_a bilan bog'lanishi Brensted tenglamasida ifodalanadi:

$$K = G_a K_a^\alpha. \quad (\text{XII. 13})$$

G_a va α — turg'un sonlar bo'lib, odatda, 1 dan kichik bo'ladi.

Xuddi shunday asos katalizda katalitik tezlik konstantasi (k_b) uchun ham keltirish mumkin:

$$\left. \begin{aligned} K_b &= G_b K_a^b \\ \lg K_b &= \lg G_b + \lg K_a^b \end{aligned} \right\} \quad (\text{XII. 14})$$

G_b^β — turg'un kattaliklar;

K_a^b — katalizatorning asoslik konstantasi (asos katalizatorning ionlanish-dissotsilanish konstantasi).

XII.2. GETEROGEN KATALIZ

Qattiq katalizator ishtirokida gazsimon moddalar reaksiyasi birin-ketin boradigan quyidagi 5 bosqichdan iborat; 1) reaksiyaga kirishuvchi moddalarning katalizator yuzasiga kelishi; 2) moddalarning katalizator yuzasida adsorbiyasi; 3) katalizator yuzasida reaksiyaning borishi; 4) reaksiya mahsulotlarining katalizator yuzasidan ketishi (desorbsiya); 5) mahsulotlarning katalizator yuzasidan gaz faza hajmiga o'tishi.

Reaksiya tezligi eng sekin boruvchi bosqichning tezligiga teng bo'ladi. Odatda, bunday bosqich katalizator yuzasida boradigan reaksiyadir.

Agar reaksiya statistik sharoitda (o'zgaras hajmdagi og'zi yopiq idishda) olib borilsa va 3-bosqich eng sekin boradigan jarayon bo'lsa, monomolekular reaksiyaning tezlik konstantasi quyidagicha ifodalanadi:

$$k = \frac{V}{RTSbt} \left[2,3 \lg \frac{P^\circ}{P} + b(P^\circ - P) \right]. \quad (\text{XII. 15})$$

Bu tenglamada P° , P — reaksiyaga kirishuvchi moddaning boshlang'ich va t vaqtdagi parsial bosimi, S — katalizatorning yuzasi, b — Lengmyur doimiysi, t — vaqt, V — idish hajmidir.

Agar moddaning bosimi kichik hamda adsorbsialanishi sust holda va $P \leq 1$ bo'lsa:

$$V = kbP. \quad (\text{XII.16})$$

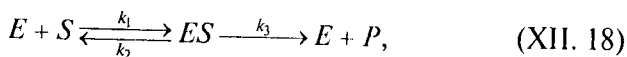
Agar reaksiya moddaning parsial bosimiga nisbatan birinchi tartibli bo'lsa:

$$P \geq 1 \text{ bo'ladi va } V = k \text{ ga tengdir.} \quad (\text{XII.17})$$

XII.3. FERMENTATIV KATALIZ

Fermentlar asosan oqsillardan iborat bo'lib, ular noorganik katalizatorlardan ikki xususiyati bilan farqlanadi. Birinchidan, juda yuqori tanlovchanlik xossasiga ega bo'lib, ma'lum bir ferment faqat ma'lum reaksiyanigina tezlatadi (ba'zan faqat ma'lum sharoitda). Ikkinchidan, ular juda katta katalitik qobiliyatga ega bo'lib, juda oz miqdorda (10^{-7} – 10^{-9} mol) qo'shilganda ham reaksiya tezligini minglab, hatto 10^{10} marta tezlatadi. Bu kataliz gomogen kataliz sinfiga mansub bo'lib, gomogen-geterogen katalizning asosiy qonunlariga bo'ysunadi. Ferment kataliz mexanizmi juda murakkab bo'lganligidan, eng sodda ikki bosqichli reaksiyani bayon etish bilan chegaralanadi.

Ferment substrat (reaksiyaga kirishuvchi moddalar) bilan birikib, *ferment-substrat kompleksi* hosil qiladi va ikkinchi bosqichda bu kompleks parchalanib, mahsulot va ferment hosil bo'ladi:



E , S , P — ferment, substrat va reaksiya mahsuloti. Ferment-substrat kompleksi (ES) ning dissotsilanish konstantasi:

$$k_3 = \frac{[E][S]}{[ES]}. \quad (\text{XII.19})$$

Odatda, ferment konsentratsiyasi substrat konsentratsiyasiga nisbatan ko'p marotaba kam bo'ladi $[S]_0 \gg [E]_0$.

$[S]_0$, $[E]_0$ — boshlang'ich konsentratsiyalar.

$$[E]_0 = [E] + [ES], \quad (\text{XII. 20})$$

E — ma'lum vaqtda reaksiyaga kirishmagan ferment miqdori.

Odatda, bunday reaksiyalarda ferment-substrat kompleksining ajralish tezligi kichik bo'ladi va reaksiyaning tezligini belgilaydi:

$$V = k_3[ES], \quad (\text{XII. 21})$$

Yuqoridagi tenglamalar birgalikda hal qilinsa:

$$V = \frac{k_3[E]_0[S]}{k_3 + [S]} \quad (\text{XII.22})$$

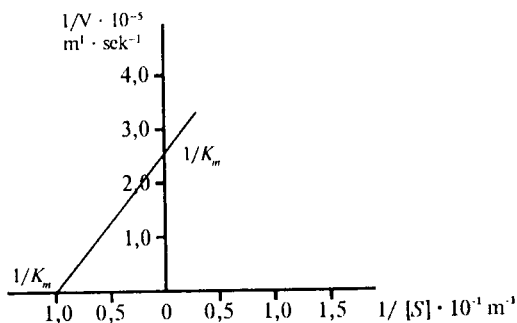
reaksiya boshida substrat kam reaksiyaga kirishganda $[S]_0 = [S]$ deb qabul qilish mumkin. Bunda (XII. 22) tenglama quyidagi ko'rinishda bo'ladi:

$$V = \frac{k_3[E]_0[S]_0}{k_3 + [S]_0}. \quad (\text{XII.23})$$

Agar k_2 ; k_3 effektiv kattaliklar bo'lsa, ya'ni tezlik pH ga, ingibitor-aktivatorga va hokazolarga bog'liq bo'lsa, ular katalitik tezlik konstantasi k_k va Mixaelis doimiyligi (k_M) deyiladi.

$k_k[E]_0$ — o'lchami tezlik bo'lganligidan maksimal tezlik V_m deyiladi va (XII.22) tenglama quyidagicha ifodalanadi:

$$V = \frac{V_m[S]_0}{k_m + [S]_0} \quad (\text{XII.24})$$



XII.1-rasm.

(XII. 23) va (XII.24) tenglamalar Mixaelis-Menten tenglamasi deb ataladi.

Tajribada reaksiya tezligi (V va k_m , V_m) larni aniqlash uchun (XII. 24) tenglamani quyidagicha yozish mumkin:

$$\frac{1}{V} = \frac{k_m[S]_0}{V_m + [S]_0} \quad (\text{XII. 25})$$

va

$$\frac{1}{V} = \frac{1}{V_m} + \frac{k_m}{V_m} \cdot \frac{1}{[S]_0} \quad (\text{XII. 26})$$

Agar koordinatalar sistemasining abssissalar o'qiga $1/[S]$, ordinatalar o'qiga $\frac{1}{V}$ qo'yilsa, XII.1-rasmda tasvirlanganidek to'g'ri chiziqli olinadi.

$\frac{1}{V} = 0$ bo'lganda $\frac{1}{K_m} = \frac{1}{[S]_0}$ va $\frac{1}{[S]} = 0$ bo'lganda $\frac{1}{V_m} = \frac{1}{V}$ bo'ladi. Bu nuqtalarning qiymati rasmda ko'rsatilgan.

MASALALAR YECHISHIGA DOIR MISOLLAR

1. A moddaning halqalanish (sikllanish) tezligi pH qiymatiga bog'liq. Quyida pH o'zgarishi bilan K_a ning ham o'zgarishi keltirilgan. Chin tezlik konstantasi k va pK_a ni toping.

pH	2,0	2,8	3,2	3,6	3,8	4,1	4,3	4,4	4,7	5,0
$k_{ef} \cdot 10^{-3}$ sek ⁻¹	15,50	14,50	13,60	12,10	9,60	6,50	5,00	4,18	2,70	1,42

Y e c h i s h . (XII.10) tenglamaga muvofiq:

$$K_{ef} = K - \frac{k_{ef}C_{n+}}{K_a}$$

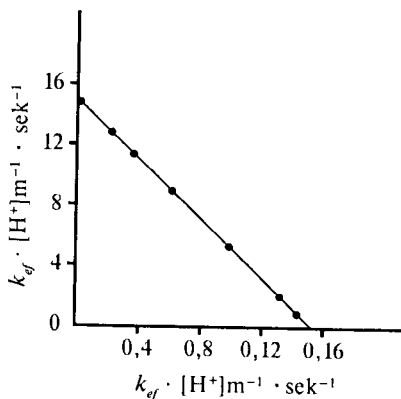
Demak, koordinatalarning abssissa o'qiga $K_{ef}[H^+]$ va ordinata o'qiga K_{ef} qo'yilsa, to'g'ri chiziq olinadi, chiziqning ordinata o'qi bilan kesishgan nuqtasi $\frac{1}{K}$, abssissa o'qi bilan kesishgan nuqtasi $\frac{1}{K_a}$ ga teng bo'ladi (XII. 2-rasm).

2. $A \rightarrow B$ reaksiyasi kinetikasini o'rganganda tezlik konstantasi ion kuchi I bilan o'zgarishi quyidagicha bo'lgan:

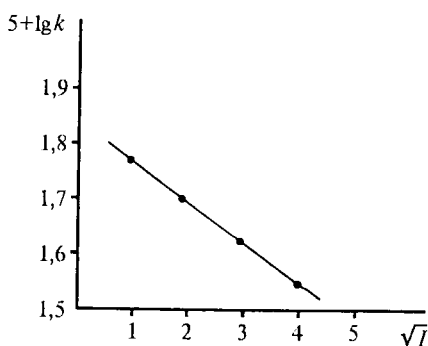
I	2,24	5,61	8,10	11,22	11,73	16,90
$5 + \lg k$	1,7640	1,7130	1,6300	1,6467	0,6418	1,5900

Ion kuchi $I = 1$ bo'lganda tezlik konstantasi k_0 qanchaga teng bo'ladi?

Y e c h i s h . (XII. 1) tenglamadan foydalanamiz. Ordinatalar o'qiga $5 + \lg k$, abssissalar o'qiga esa $\sqrt{I}$ ning qiymatlarini qo'yib, chiziq



XII.2-rasm.



XII.3-rasm.

$\sqrt{I} = 0$ teng bo'lgunga qadar fikran davom ettiriladi (XIII. 3-rasm) va $\sqrt{I} = 0$ ga to'g'ri kelgan ordinata o'qidan k_0 aniqlanadi. $\sqrt{I} = 1$ teng bo'lganda $(5 + \lg k_0) = 1,858$ ga teng bo'ladi va demak, $k_0 = 7,21 \cdot 10^{-4}$ bo'ladi.

3. Biron moddaning metil efiri gidrolizida ferment A katalizator bo'ladi. Bu reaksiyaning kinetikasi 298,2 K da o'rganilganda boshlang'ich tezlik (V_0) substratning (S) miqdori o'zgarishi bilan quyidagicha o'zgargan:

$[S]_0$	0,200	0,124	0,124	0,091	0,091	0,071	0,071	0,060	0,060
$V_0 \cdot 10^6 \text{ sek}^{-1}$	4,57	3,83	3,84	3,33	3,31	2,97	2,93	2,67	2,74

V_m , k_{kam} va k_m ning qiymatini hisoblab toping.

Yechish. (XII. 26) tenglamaga muvofiq ma'lumotlar $\left(\frac{1}{V_m} = \frac{1}{[S]_0}\right)$ koordinatalar sistemasiga qo'yib chiqiladi va grafikdan

kinetik faktorlarni topamiz. Bunda quyidagi natijalar olindi:

$$V_m = 6,58 \cdot 10^{-6} \text{ m} \cdot \text{sek}^{-1}, k_{kam} = 0,173 \text{ sek}^{-1}, k_m = 8,77 \cdot 10^{-2} \text{ m}.$$

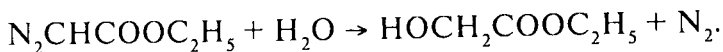
MASALALAR

1. A moddaning izomerlanishida gidroksil ioni katalizator bo'ladi. Bu reaksiyaning kinetikasi o'rganilganda quyidagi natijalar olingan.

pH	0,48	0,89	1,01	1,44	1,78	2,20	3,51
$k_{eff} \cdot 10^7 \text{ sek}^{-1}$	0,2	0,7	1,0	1,7	2,4	3,2	3,9

Bu reaksiya uchun pK_v va k_1 ning qiymatlarini aniqlang.

2. Diazosirka kislota etil efirining gidrolizida vodorod ioni katalizatoridir:



Bu reaksiyaning effektiv konstantasi k_{ef} vodorod ionining konsentratsiyasi o'zgarishi bilan quyidagicha o'zgaradi:

$[H_3O^+]$, mol/l	0,00046	0,00087	0,00158	0,00323
k , l/mol · sek	0,0218	0,0320	0,0578	0,1218

Grafik usulidan foydalanib, reaksiyaning tezlik konstantasi k_{H^+} ni toping.

3. Glukozaning mutarotatsiya reaksiyasi birinchi tartibli reaksiya bo'lib, bir vaqtda vodorod va gidroksil ionlari katalizator bo'ladi. 291 K da 0,02 mol/l natriy asetat eritmasi va turli konsentratsiyada sirka kislota bilan olib borilgan tajribada quyidagi natijalar olingan:

$[CH_3COOH]$, mol/l	0,020	0,105	0,190
$k \cdot 10^4$, min ⁻¹	1,36	1,40	1,46

k_0 , k_{OH} qiymatlarini toping. Bu sharoitda $k_{H^+ + [H_3O^+]}$ juda kichik bo'lganligidan uni hisobga olmasa ham bo'ladi.

4. Glukozaning mutarotatsiya reaksiyasi glukozaga nisbatan birinchi tartibli reaksiya bo'lib, reaksiya perxlorat $HClO_4$ katalizatori ishtirokida olib borilgan. $HClO_4$ kuchli kislota bo'lganligidan H^+ konsentratsiyasi kislota konsentratsiyasiga teng bo'ladi. Perxlorat ionining ta'siri juda kam bo'lgani uchun uni e'tiborga olmasa ham bo'ladi. Tezlik konstantasining o'zgarishi $HClO_4$ ning konsentratsiyasi o'zgarishi bilan quyidagicha bo'lgan:

$[HClO_4]$, mol/l	0,0010	0,0048	0,0099	0,0192	0,0301	0,0400
$k \cdot 20^4$, min	1,25	1,38	1,53	1,90	2,13	2,59

k_0 , k_{H^+} qiymatlarini toping.

5. 0,5 mol/l sirka kislota va 0,3 mol/l natriy asetat eritmasi tayyorlangan. Sirka kislotaning dissotsilanish konstantasi $k_a = 1,8 \cdot 10^{-5}$, Brensted tenglamasidagi α —kislotali katalizda $k_a = 0$. Vodorod ioni bo'yicha sirka kislota va suvning reaksiyaga kirishganini (% hisobida) aniqlang.

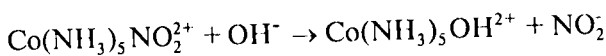
6. Ion kuchi 0,01 dan 0,04 gacha o'zgarganda reaksiyaning tezlik konstantasi qanchaga o'zgaradi?

7. Natriy persulfat bilan yod o'rtasidagi reaksiyaning tezlik konstantasi ion kuchi (I) o'zgarishi bilan quyidagicha o'zgaradi:

I mol/l	0,00245	0,00365	0,00445	0,00643	0,00848	0,11245
$k, l/mol \cdot sek$	1,05	1,12	1,16	1,18	1,26	1,39

(XI. 1) tenglama asosida grafik usuldan Z^+ va Z^- ning qiymatini toping. Reaksiya tezligi persulfat ionlar va yod o'rtasidagi reaksiya tezligiga teng bo'lsa, persulfat ioni qanday zaryadga ega ($1+$ yoki -1) bo'ladi?

8. Quyidagi reaksiyaning



konstantasi o'rganilganda, ion kuchi $I = 5,61$ bo'lganda tezlik konstantasi $k = 5,164 \cdot 10^{-4}$ ga teng bo'lgan. Ion kuchi $I = 0$ ga teng bo'lganida tezlik konstantasi qancha bo'ladi?

9. Asetonning yodlanishi monoxlorsirka kislotasi mavjudligida tezlashadi. Monoxlorsirka kislotasining dissotsilanish muvozanat konstantasi $k_a = 1,41 \cdot 10^{-3}$ ga teng. Brensted tenglamasi bu reaksiya uchun quyidagi ko'rinishda bo'ladi: $k = 7,90 \cdot 10^{-4}$. Reaksiyaning k_{H^+} tezlik konstantasini aniqlang.

10. Reaksiya 400 K da olib borilganda aktivlanish energiyasi $E_1 = 29,824 \text{ kJ/mol}$, qattiq katalizator mavjudligida aktivlanish energiyasi $E_2 = 26000 \text{ J/mol}$ ga teng bo'lgan. Arrenius tenglamasidagi eksponensial oldidagi k_0 ikkala holda ham bir xil bo'lgan. Katalizator reaksiya tezligini necha marta orttiradi?

11. Ammiakning parchalanishi $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ katalizatorsiz olib borilganda 298 K da aktivlanish energiyasi $E = 320 \text{ kJ/mol}$ ga teng. Volfram (W) katalizator mavjudligida shu haroratda $E_w = 163 \text{ kJ/mol}$ ga, M_0 katalizator ishtirokida $E_{\text{M}_0} = 121,3 \text{ kJ/mol}$, temir Fe katalizator mavjudligida $E_{\text{Fe}} = 125,5 \text{ kJ/mol}$ ga teng bo'lgan. Osmiy Os katalizatorida $E_{\text{Os}} = 197 \text{ kJ/mol}$ ga teng bo'lgan. Katalizator mavjudligida reaksiya necha marta tezlashganligi aniqlansin, katalizator aktivlik qatori tuzilsin, aktiv kompleks aktivlanish entalpiyasi ΔH hisoblansin.

12. Etil spirti ajralish reaksiyasi $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ tezligi Al_2O_3 katalizator ishtirokida 650 K da $k_{\text{ef}} = 2,34 \text{ sek}^{-1}$ ga teng bo'lgan. Tezlik konstantasi harorat bilan $\lg k = 6,06 - 4230/T$ tenglamasiga muvofiq o'zgaradi. Katalizator yuzasida boradigan reaksiyaning aktivlanish energiyasini aniqlang.

13. Quyidagi jadvalda N benzoil-1 amino yog' kislota metil efirining ferment-ximtripsin ta'sirida gidroliz reaksiyasi kinetikasi ma'lumotlari keltirilgan. k_{kat} , k_m larning qiymatlarini toping.

$[S]_0 \cdot 10^2 \text{ m}$	2,24	2,24	1,49	1,49	1,12	1,12	0,90	0,90	0,75	0,75
$V_0 \cdot 10^2 \text{ m/sek}$	4,23	4,31	3,52	3,10	3,10	3,12	2,71	2,43	2,43	2,40

14. α ximtripsin fermenti bilan β efiri gidrolizlanish reaksiyasining k_{kat} va k_m qiymatlarini quyidagi jadvalda keltirilgan ma'lumotdan foydalanib toping.

$[S]_0 \cdot 10^2 \text{ m}$	4,00	4,00	2,00	2,00	1,33	1,33	1,00	1,00	0,80	0,80
$V_0 \cdot 10^2 \text{ m/sek}$	9,7	10,0	7,77	7,87	0,51	6,41	5,50	5,51	4,80	4,72

15. Jadvalda keltirilgan ma'lumotlardan foydalanib, b efirining α -ximotropsin katalizatori ta'sirida gidrolizlanish reaksiyasining kinetik parametrlari k_{kat} , k_m qiymatlarini toping.

$[S]_0 \cdot 10^2 \text{ m}$	1,5-30	1,5-30	1,7-65	0,510	0,51-0	0,383	0,38-3	0,38-3	0,30-6	0,30-6
$V_0 \cdot 10^2 \text{ m/sek}$	4,94	4,98	4,20	4,30	3,74	3,70	3,02	2,98	3,32	3,28

16. Quyidagi jadvalda keltirilgan ma'lumotlardan foydalanib, efirning ferment — α -ximotropsin katalizatori mavjudligida borgan gidroliz reaksiyasining kinetik kattaliklari k_{kat} , k_m ni toping.

$[S]_0 \cdot 10^4 \text{ m}$	3,6	1,8	1,2	0,90	0,72
$V_0 \cdot 10^7 \text{ m/sek}$	1,94	1,84	1,75	1,67	1,50

17. A moddaning gidrolizlanish reaksiyasini lizosin fermenti tezlatadi. Jadvalda keltirilgan ma'lumotlardan foydalanib, k_{kat} , k_m qiymatlarini toping.

$[S]_0 \cdot 10^2 \text{ m}$	1,00	1,00	0,08-0	0,80	0,67	0,65	0,55	0,50
$V_0 \cdot 10^6 \text{ m/sek}^{-1}$	3,25	3,41	2,86	2,79	2,45	2,15	2,13	2,01

ILOVALAR

Ba'zi moddalarning standart termodinamik kattaliklari

1-jadval

№	Modda	$\Delta I P_{298}^0$ kJ/mol	S_{298}^0 J/mol · grad	Issiqlik sig'imi, J/mol · grad				
				$C_p = f(T)$ ko'effitsiyentlari				
				a	$b \times 10^{-3}$	$c \times 10^{-5}$	$d \times 10^6$	$e \times 10^9$
1	2	3	4	5	6	7	8	9
1	H ₂	0	170,6	27,28	3,26	0,502	τ	—
2	O ₂	0	205,03	31,46	3,39	3,77	—	—
3	S(b)	0	31,88	14,98	26,11	—	—	—
4	N ₂ (g)	0	191,5	27,87	4,27	—	—	—
5	Cl ₂ (g)	0	223,0	36,69	1,05	- 2,52	—	—
6	CO	- 110,5	197,4	28,41	4,10	- 0,46	—	—
7	CO ₂	- 393,51	213,6	44,14	9,04	- 8,53	—	—
8	CaO	- 635,1	39,7	49,63	4,52	- 6,05	—	—
9	Ca(OH) ₂	- 986,2	83,4	105,2	12,0	- 19,0	—	—
10	CaCO ₃	- 1206	92,9	104,5	21,92	- 25,94	—	—
11	HCl(g)	- 92,30	186,70	26,53	4,60	- 1,09	—	—
12	H ₂ O(g)	- 241,84	188,74	30,00	10,71	0,33	—	—
13	H ₂ O(S)	- 285,84	105,86	29,37	15,40	—	—	—
14	MgO	- 601,24	26,94	42,59	7,28	- 6,19	—	—
15	Mg(OH) ₂	- 924,66	63,14	54,56	06,11	—	—	—
16	NH ₃	- 46,19	192,5	29,80	25,48	- 1,67	—	—
17	NH ₄ Cl	- 315,39	94,36	49,37	133,89	—	—	—
18	NO	90,37	220,0	45,69	8,62	- 8,53	—	—
19	NO ₂	33,89	240,45	42,93	8,54	- 6,74	—	—
20	N ₂ O ₄	9,37	304,3	83,89	39,75	- 14,9	—	—
21	SO ₂	- 296,9	248,1	42,55	12,55	- 5,65	—	—
22	SO ₃	- 395,2	256,23	57,32	26,86	- 13,05	—	—
23	SO ₂ Cl ₂ (g)	- 358,7	311,3	53,72	72,50	—	—	—
24	SO ₂ Cl ₂ (s)	- 389,1	217,2	—	—	—	—	—
25	COCl ₂ (g)	- 223,0	289,2	67,16	12,11	—	—	—
26	CH ₄	- 74,85	186,19	17,45	60,46	—	1,117	- 7,20
27	C ₂ H ₂	226,75	200,8	23,40	85,77	—	- 58,34	15,87
28	C ₂ H ₄	52,28	219,4	4,196	154,59	—	- 81,09	16,82
29	C ₂ H ₆	- 84,67	229,5	4,494	182,26	—	- 74,86	10,3

1	2	3	4	5	6	7	8	9
30	$C_6H_6(g)$	12,93	269,2	- 33,90	471,87	—	- 298,3- 4	70,34
31	$C_6H_6(S)$	- 49,04	173,2	59,50	255,02	—	—	—
32	HCOH	- 115,9	218,8	18,82	53,38	—	- 15,61	—
33	$CH_3OH(S)$	- 238,7	726,7	—	—	—	—	—
34	$CH_3OH(g)$	- 201,2	239,7	15,28	105,2	—	- 31,04	—
35	$C_2H_5OH(S)$	- 27,76	160,7	—	—	—	—	—
36	$C_2H_5OH(g)$	- 235,3	282,0	10,07	212,7	—	- 108,6	21,9
37	CH_3CHO	- 166,0	264,2	13,0	153,5	—	- 53,7	—
38	$CH_3COOH(S)$	- 484,9	159,8	—	—	—	—	—
39	$CH_3COOH(g)$	- 437,4	282,5	5,50	243,5	—	- 151,9	36,8
40	CH_3COCH_3	247,4	210	—	—	—	—	—
41	$CH_3COOH_3(g)$	- 216,4	294,9	22,47	201,8	—	- 63,5	—
42	$C_6H_5CH_3(S)$	50,00	319,7	- 33,88	557,0	—	- 342,4	79,67
43	$C_6H_5CH_3(g)$	8,08	219	—	—	—	—	—
44	$C_6H_4(CH_3)_2(g)$	17,27	357,2	- 27,38	620,9	—	- 363,9	81,33
45	$C_6H_4(CH_3)_2(g)$	- 24,4	246,0	—	—	—	—	—

ΔH_{298}^0 — standart hosil bo'lish issiqlik effekti; S_{298}^0 — entropiya mutlaq qiymati; C_p — o'zgarmas bosimdagi issiqlik sig'imi.

C_p ning haroratga bog'liqlik tenglamalari:

$$C_p = a + bt + c/T^2; \quad C_p = a + bt + cT^2 + dt^3$$

2-jadval

Ba'zi moddalarning izobarik issiqlik sig'imi (C_p)

№	Modda	C_p , J/mol · grad	№	Modda	C_p , J/mol · grad
1	Ag	25,48	8	Zn	25,48
2	Cl_2	33,84	9	CO	29,15
3	F_2	31,32	10	CO_2	37,13
4	H_2	28,83	11	H_2O	75,31
5	I_2	39,90	12	CH_4	35,79
6	N_2	29,19	13	C_2H_6	32,70
7	O_2	29,36			

Ba'zi moddalarning standart hosil bo'lish issiqlik (ΔI_{298}^0)
effekti va mutlaq entropiyasi qiymatlari (ΔS_{298}^0)

N _o	Modda	ΔI_{298}^0 kJ/mol · grad	S_{298}^0 J/mol · grad	N _o	Modda	ΔI_{298}^0 kJ/mol · grad	S_{298}^0 J/mol · grad
1	Ag	0	48	10	Na ₂ CO ₃	- 4077	2172
2	F ₂	0	202,9	11	PCl ₃	- 277,0	311,7
3	H ₂	31,32	31,32	12	PCl ₅	- 369,45	302,9
4	I ₂	210,58	28,83	13	MgCO ₃	- 1096,21	65,69
5	AgNO ₃	- 120,7	140,9	14	ZnO	- 349,0	435
6	COS	- 137,2	231,5	15	ZnS	- 201,0	57,7
7	Cl ₂	115,3	237,8	16	HI	25,94	200,30
8	H ₂ S	- 20,15	205,64	17	C ₆ H ₁₂	- 123,1	298,2
9	NaHCO ₃	- 917,4	102,1				

Chiziqli garmonik ossillator uchun Eynshteynning
termodinamik funksiyalari

θ/T	CE	$\frac{U-U_0}{T} = \frac{1}{T} \int_0^T C dT$	$-\frac{F-U_0}{T} = -\int_0^T \frac{dT}{T^2} \int_0^T C dT$	$S = \frac{U-F}{T}$	CE	$\frac{U-U_0}{T} = \frac{1}{T} \int_0^T C dT$	$-\frac{F-U_0}{T} = -\int_0^T \frac{dT}{T^2} \int_0^T C dT$	$S = \frac{U-F}{T}$
	J/g·atom				kal/g·atom			
1	2	3	4	5	6	7	8	9
0	8,309	8,309	—	—	1,986	1,986	—	—
0,1	8,297	7,899	19,539	27,447	1,983	1,888	4,67	6,56
0,15	8,288	7,703	16,276	23,974	1,981	1,841	3,89	5,730
0,20	8,280	7,368	14,184	21,715	1,979	1,761	3,39	5,190
0,25	8,268	7,309	12,510	19,832	1,976	1,747	2,99	4,740
0,30	8,259	7,121	11,213	18,368	1,974	1,702	2,68	4,39
0,35	8,230	6,941	10,125	17,071	1,967	1,659	2,42	4,080
0,40	8,200	6,757	9,205	15,983	1,960	1,615	2,20	3,820
0,45	8,167	6,577	8,452	15,062	1,952	1,572	2,02	3,600

1	2	3	4	5	6	7	8	9
0,50	8,138	6,406	7,740	14,142	1,945	1,531	1,85	3,380
0,55	8,109	6,234	7,150	13,389	1,938	1,490	1,709	3,200
0,60	8,067	6,063	6,615	12,682	1,928	1,449	1,581	3,031
0,65	8,025	5,899	6,138	12,037	1,918	1,410	1,467	2,877
0,70	7,983	5,736	5,707	11,447	1,908	1,371	1,364	2,736
0,75	7,933	5,581	5,314	10,895	1,896	1,334	1,270	2,604
0,80	7,883	5,423	4,958	10,385	1,884	1,297	1,185	2,482
0,85	7,828	5,272	4,636	9,912	1,871	1,260	1,108	2,369
0,90	7,774	5,121	4,339	9,464	1,858	1,224	1,037	2,262
0,95	7,715	4,983	4,067	9,046	1,844	1,191	0,972	2,162
1,00	7,652	4,837	3,812	8,652	1,829	1,156	0,911	2,068
1,05	7,590	4,699	3,582	8,280	1,814	1,123	0,856	1,979
1,10	7,523	4,561	3,364	7,929	1,798	1,090	0,804	1,859
1,15	7,456	4,427	3,163	7,845	1,782	1,058	0,756	1,815
1,20	7,385	4,297	2,979	7,280	1,765	1,027	0,712	1,740
1,25	7,309	4,171	2,807	6,979	1,747	0,997	0,671	1,668
1,30	7,234	4,050	2,644	6,694	1,729	0,968	0,632	1,600
1,40	7,079	3,812	2,356	6,012	1,692	0,911	0,563	1,437
1,45	7,000	3,694	2,222	5,916	1,673	0,883	0,531	1,414
1,50	6,941	3,582	2,100	5,682	1,659	0,856	0,502	1,358
1,55	6,832	3,468	1,983	5,456	1,633	0,829	0,474	1,304
1,60	6,745	3,364	1,874	5,238	1,612	0,804	0,448	1,252
1,65	6,661	3,259	1,774	5,033	1,592	0,779	0,424	1,252
1,70	6,569	3,159	1,678	4,837	1,570	0,755	0,401	1,156
1,75	6,481	3,058	1,586	4,648	1,549	0,731	0,379	1,111
1,80	6,389	2,962	1,502	4,464	1,527	0,708	0,359	1,067
1,85	6,297	2,870	1,422	4,293	1,505	0,686	0,340	1,026
1,90	6,205	2,778	1,347	4,125	1,483	0,664	0,322	0,986
1,95	6,113	2,648	1,276	3,966	1,461	0,633	0,305	0,948
2,00	6,021	2,602	1,209	3,812	1,439	0,622	0,289	0,911
2,10	5,828	2,435	1,084	3,523	1,393	0,582	0,259	0,842
2,20	5,640	2,280	0,975	3,255	1,348	0,545	0,233	0,778
2,30	5,448	2,134	0,879	3,008	1,302	0,510	0,210	0,719
2,40	5,255	1,992	0,791	2,782	1,256	0,476	0,189	0,665
2,50	5,063	1,858	0,711	2,569	1,210	0,444	0,170	0,614

1	2	3	4	5	6	7	8	9
2,20	5,640	2,280	0,975	3,255	1,348	0,545	0,233	0,778
2,30	5,448	2,134	0,879	3,008	1,302	0,510	0,210	0,719
2,40	5,255	1,992	0,791	2,782	1,256	0,476	0,189	0,665
2,50	5,063	1,858	0,711	2,569	1,210	0,444	0,170	0,614
2,60	4,870	1,732	0,640	2,377	1,164	0,414	0,153	0,568
2,70	4,682	1,615	0,577	2,197	1,119	0,386	0,138	0,525
2,80	4,494	1,506	0,523	2,029	1,074	0,360	0,125	0,485
2,90	4,310	1,406	0,469	1,874	1,030	0,336	0,112	0,448
3,00	4,125	1,305	0,427	1,732	0,986	0,312	0,102	0,414
3,10	3,946	1,218	0,385	1,598	0,943	0,291	0,092	0,382
3,20	3,770	1,130	0,347	1,477	0,901	0,270	0,083	0,353
3,30	3,598	1,050	0,314	1,364	0,860	0,251	0,075	0,326
3,40	3,431	0,975	0,280	1,259	0,820	0,233	0,067	0,301
3,50	3,268	0,908	0,255	1,159	0,781	0,217	0,061	0,277
3,60	3,113	0,841	0,230	1,071	0,744	0,201	0,055	0,256
3,70	2,958	0,782	0,209	0,987	0,707	0,187	0,050	0,236
3,80	2,812	0,724	0,188	0,912	0,672	0,173	0,045	0,218
3,90	2,665	0,669	0,172	0,841	0,637	0,160	0,041	0,201
4,00	2,527	0,619	0,155	0,774	0,604	0,148	0,037	0,185
4,20	2,268	0,531	0,126	0,657	0,542	0,127	0,030	0,157
4,40	2,025	0,456	0,105	0,556	0,484	0,109	0,025	0,133
4,60	1,803	0,3878	0,084	0,473	0,431	0,0927	0,020	0,113
4,80	1,602	0,3305	0,067	0,402	0,383	0,0790	0,016	0,096
5,00	1,418	0,2816	0,058	0,339	0,0673	0,014	0,081	5,20
5,20	1,255	0,2397	0,046	0,284	0,300	0,0573	0,011	0,068
5,40	1,096	0,2038	0,038	0,243	0,262	0,0487	0,009	0,058
5,60	0,971	0,1728	0,029	0,205	0,232	0,0413	0,007	0,049
5,80	0,854	0,1477	0,025	0,172	0,204	0,0353	0,006	0,041
6,00	0,745	0,1243	0,021	0,146	0,178	0,0297	0,005	0,035
6,40	0,569	0,1050	0,012	0,100	0,136	0,0251	0,003	0,024
6,80	0,431	0,0632	0,008	0,071	0,103	0,0151	0,002	0,017
7,20	0,322	0,0448	0,004	0,058	0,077	0,0107	0,001	0,014
7,60	0,238	0,0318	0,004	0,038	0,057	0,0076	0,001	0,014
8,00	0,1786	0,0222	0,004	0,025	0,0427	0,0053	0,001	0,006

Davomi

1	2	3	4	5	6	7	8	9
8,40	0,134	0,0159	0,000	0,017	0,032	0,0038	0,000	0,004
8,80	0,096	0,0126	—	0,012	0,023	0,0030	—	0,003
9,20	0,071	0,0075	—	0,008	0,017	0,0018	—	0,002
9,60	0,050	0,0054	—	0,004	0,012	0,0013	—	0,001
10,00	0,038	0,0038	—	—	0,009	0,0009	—	—
11	0,017	0,0017	—	—	0,004	0,0004	—	—
12	0,0071	0,0004	—	—	0,0017	0,0001	—	—
13	0,0029	—	—	—	0,0007	—	—	—

5-jadval

Ba'zi moddalar uchun $\frac{G^0 - H^0}{T}$ va ΔH_0

funksiyalarning qiymatlari

№	Modda	$\frac{G^0 - H^0}{T}$, J/mol · grad						ΔH_0 , kJ/mol
		298,15 K	500 K	800 K	1000 K	1500 K	2000 K	
1	Cl ₂	192,200	208,568	224,254	231,944	246,200	256,663	0
2	H ₂	102,182	116,922	130,482	136,963	148,904	157,603	0
3	N ₂	162,423	177,473	191,276	197,932	210,302	219,567	0
4	O ₂	175,929	191,056	205,171	212,09	225,111	234,722	0
5	CO	168,469	183,527	197,368	204,079	216,643	225,907	- 113,880
6	CO ₂	182,263	192,439	217,158	226,406	244,689	258,759	- 393,229
7	COCl ₂	240,433	264,830	290,817	304,399	330,912	350,960	- 215,932
8	HCl	157,812	172,816	186,523	193,108	205,347	214,346	- 92,140
9	H ₂ O	155,507	172,770	188,845	196,744	211,853	223,392	- 238,906
10	NH ₃	158,975	170,816	194,455	203,648	222,166	237,028	- 39,221
11	NO	179,816	195,631	210,020	216,970	229,932	239,434	89,872
12	NO ₂	205,878	224,191	242,433	251,827	270,213	284,253	36,263
13	SO ₂	212,710	231,760	250,868	260,672	279,663	293,972	- 258,937
14	SO ₃	217,777	240,057	264,065	276,838	302,168	321,525	- 453,947
15	CH ₄	152,520	170,527	189,008	190,313	220,944	239,015	- 66,965
16	C ₂ H ₄	183,987	203,794	226,316	239,162	266,776	289,809	59,609
17	C ₂ H ₆	189,410	212,42	230,70	255,68	290,62	—	- 69,340
18	CH ₃ OH	201,376	222,34	244,97	252,65	—	—	- 190,380
19	HCOH	185,16	203,00	220,90	230,54	250,25	—	- 112,148

Ba'zi tuzlarning suvda integral erish issiqligi

№	1 kg H ₂ O dagi m, tuz moli	LiCl		LiBr		NaCl		NaBr		NaJ		KCl		KBr	
		kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	1	-37,13	-8,875	-49,02	-11,717	3,89	0,930	-0,63	-0,150	-7,57	-1,81	17,23	4,119	15	16
2	0,01	-36,97	-8,835	-48,91	-11,690	4,06	0,970	-0,30	-0,120	-7,41	-1,77	17,39	4,157	20,04	7,790
3	0,02	-36,86	-8,810	-48,87	-11,680	4,10	0,980	-0,42	-0,100	-7,36	-1,76	17,44	4,168	20,25	4,820
4	0,05	-36,71	-8,775	-48,74	-11,650	4,18	1,000	-0,31	-0,075	-7,24	-1,73	17,51	4,185	20,29	4,840
5	0,1	-36,48	-8,720	-48,62	-11,620	4,25	1,015	-0,29	-0,070	-7,20	-1,72	17,55	4,195	20,33	4,850
6	0,2	-36,34	-8,685	-48,39	-11,565	4,27	1,020	-0,27	-0,065	-7,15	-1,71	17,57	4,199	20,39	4,860
7	0,3	-36,19	-8,650	-48,28	-11,540	4,25	1,015	-0,29	-0,070	-7,24	-1,73	17,55	4,194	20,25	4,840
8	0,4	-36,07	-8,620	-48,20	-11,520	4,16	0,995	-0,40	-0,095	-7,32	-1,75	17,50	4,182	20,15	4,815
9	0,5	-35,98	-8,600	-48,12	-11,500	4,10	0,980	-0,44	-0,105	-7,41	-1,77	17,43	4,166	20,04	4,790
10	1,0	-35,65	-8,520	-47,74	-11,410	3,79	0,905	-0,86	-0,205	-7,82	-2,06	16,72	3,995	18,68	4,465
11	2,0	-35,15	-8,400	-47,11	-11,260	3,18	0,760	-1,65	-0,395	-8,62	-2,87	16,17	3,865	17,99	4,300
12	3,0	-34,52	-8,250	-46,53	-11,120	2,66	0,635	-2,28	-0,545	-9,37	-3,24	16,17	3,865	17,36	4,150
13	4,0	-33,89	-8,100	-46,02	-11,000	2,26	0,540	-2,78	-0,65	-10,04	-2,40	17,75	3,765	16,82	4,021
14	5,0	-33,18	-7,930	-45,50	-10,875	1,99	0,475	-3,20	-0,765	-10,54	-2,52	-	-	-	-
15	6,0	-32,43	-7,750	-44,85	-10,720	1,88	0,450	-3,47	-0,830	-10,92	-2,61	-	-	-	-
16	7,0	-31,63	-7,560	-44,22	-10,570	-	-	-3,66	-0,875	-11,13	-2,66	-	-	-	-
17	8,0	-30,79	-7,360	-43,51	-10,400	-	-	-3,70	-0,885	-11,25	-2,69	-	-	-	-
18	9,0	-29,92	-7,150	-42,80	-10,230	-	-	-3,62	-0,865	-11,25	-2,69	-	-	-	-
19	10,0	-29,00	-6,930	-41,697	-10,030	-	-	-	-	-10,71	-2,56	-	-	-	-
20	12,0	-27,03	-6,460	-35,82	-8,560	-	-	-	-	-10,71	-2,56	-	-	-	-
21	15,0	-23,97	-5,731	-36,57	-8,740	-	-	-	-	-	-	-	-	-	-
22	To'yingan eritma	-19,35	-4,624	-31,88	-7,62	1,95	0,466	-3,61	-0,863	-10,59	-2,53	15,45	3,692	16,49	3,942
To'yingan m eritman kon- sentratsiyasi, tuz moli 1 kg H ₂ O da		19,9	18,6			6,15									

№	1 kg H ₂ O dag'i m, tuz moli	KJ		KClO ₄		KNO ₃		K ₂ SO		Na ₂ Cl		NH ₄ NO ₃		CaCl ₂	
		kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
1	1	20,50	4,900	50,84	12,150	34,93	8,348	23,71	5,667	14,73	3,520	25,77	6,16	-82,93	-19,82
2	0,01	20,67	4,940	50,89	12,163	35,03	8,372	24,48	5,850	14,85	3,550	25,77	6,16	-82,68	-19,76
3	0,02	20,71	4,950	50,84	12,150	35,02	8,371	24,58	5,875	14,94	3,570	25,79	6,165	-82,38	-19,69
4	0,05	20,73	4,955	50,66	12,109	34,94	8,352	24,75	5,915	15,02	3,590	25,82	6,17	-81,25	-19,42
5	0,1	20,71	4,950	50,37	12,036	34,77	8,310	24,78	5,923	15,10	3,610	25,75	6,155	-80,88	-19,33
6	0,2	20,67	4,940	-	-	-	-	24,58	5,875	15,19	3,630	25,56	6,11	-80,50	-19,24
7	0,3	20,59	4,920	-	-	-	-	24,27	5,800	15,23	3,640	25,38	6,065	-80,25	-19,18
8	0,4	20,42	4,880	-	-	-	-	23,95	5,725	15,27	3,650	25,21	6,025	-80,02	-19,125
9	0,5	20,29	4,850	-	-	-	-	23,58	5,635	15,27	3,650	25,06	5,99	-79,83	-19,08
10	1,0	19,73	4,715	-	-	-	-	-	-	15,21	3,650	23,05	5,81	-79,04	-18,89
11	2,0	18,62	4,450	-	-	-	-	-	-	15,27	3,640	21,97	5,51	-77,74	-18,58
12	3,0	17,66	4,220	-	-	-	-	-	-	15,23	3,630	21,17	5,25	-	-
13	4,0	16,82	4,020	-	-	-	-	-	-	15,19	3,630	21,17	5,06	-	-
14	5,0	16,09	3,845	-	-	-	-	-	-	15,15	3,620	20,46	4,89	-	-
15	6,0	15,47	3,697	-	-	-	-	-	-	15,10	3,610	19,92	4,76	-	-
16	7,0	14,92	3,565	-	-	-	-	-	-	15,02	3,590	19,41	4,64	-	-
17	8,0	14,46	3,455	-	-	-	-	-	-	-	-	18,95	4,53	-	-
18	9,0	-	-	-	-	-	-	-	-	-	-	18,54	4,43	-	-
19	10,0	-	-	-	-	-	-	-	-	-	-	18,16	4,43	-	-
20	12,0	-	-	-	-	-	-	-	-	-	-	17,45	4,17	-	-
21	15,0	-	-	-	-	-	-	-	-	-	-	16,84	4,025	-	-
22	18,0	-	-	-	-	-	-	-	-	-	-	16,61	3,97	-	-
23	To'yingan eritma	-14,07	3,362	-	-	-	-	22,78	5,445	15,02	3,590	-	-	-	-
To'yingan <i>m</i> eritma, konsentratsiyasi, tuz moli 1 kg H ₂ O da		8,98		-		-		0,69		7,35					

Ishqor va kislotalarning 25°C da suvda erish integral issiqligi (ΔH_m)

7-jadval

№	1 mol kislota- tadagi H ₂ O moli soni	m kislota yoki ishqor moli	HCl		H ₂ SO ₄		HNO ₃		NH ₃ (g)		NaOH		KOH	
			kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
1	0,5	111,02	-	-	15,73	3,76	-	-	-	-	-	-	-	-
2	1	55,51	26,23	6,268	28,07	6,71	13,11	3,134	29,54	7,06	-	-	-	-
3	2	27,75	48,82	11,668	41,92	10,22	20,08	4,800	32,05	7,66	-	-	-	-
4	3	18,50	56,85	13,588	48,99	11,71	24,30	5,808	32,76	7,83	28,89	6,905	41,80	9,90
5	4	13,88	61,20	14,628	54,06	12,92	26,98	6,448	33,26	7,95	34,43	8,230	45,77	10,94
6	5	11,10	64,05	15,308	58,03	13,87	28,73	6,866	33,60	8,03	37,76	9,025	48,24	11,53
7	6	9,25	65,89	15,748	60,75	14,52	29,84	7,131	-	-	39,87	9,530	49,87	11,920
8	8	6,94	69,23	16,308	64,60	15,44	31,12	7,439	-	-	41,92	10,020	51,76	12,370
9	10	5,55	69,49	16,608	67,03	16,02	31,84	7,610	34,27	8,19	42,51	10,160	52,66	12,585
10	15	3,70	70,99	16,967	70,17	16,77	32,46	7,758	-	-	42,84	10,240	53,62	12,815
11	20	2,78	71,78	17,155	71,50	17,09	32,67	7,808	34,43	8,23	42,87	10,245	53,95	12,895
12	30	1,85	72,59	17,350	72,68	17,37	32,76	7,830	34,48	8,24	-	-	-	-
13	40	1,39	73,02	17,453	73,09	17,47	32,75	7,828	34,48	8,24	-	-	-	-
14	50	1,11	73,28	17,514	73,35	17,53	32,74	7,826	34,52	8,25	42,53	10,165	54,33	12,985
15	75	0,740	73,65	17,602	73,68	17,61	32,74	7,825	-	-	-	-	-	-
16	100	0,555	73,85	17,650	73,97	17,68	32,75	7,287	34,56	8,26	42,34	10,120	54,45	13,015
17	200	0,278	74,20	17,735	74,94	17,91	32,80	7,840	34,64	8,28	42,30	10,110	54,56	13,040
18	500	0,111	74,52	17,811	76,73	18,34	32,90	7,863	-	-	42,36	10,125	54,75	13,085
19	700	0,0793	74,61	17,832	77,57	18,54	32,94	7,873	-	-	-	-	-	-
20	1 000	0,0555	74,68	17,850	78,58	18,78	32,98	7,882	-	-	42,47	10,150	54,87	13,115
21	2 000	0,0278	74,82	17,883	80,88	19,33	33,05	7,899	-	-	42,55	10,170	55,00	13,145
22	5 000	0,0111	74,93	17,909	84,43	20,18	33,13	7,919	-	-	42,66	10,195	55,10	13,170
23	10 000	0,0056	74,99	17,924	87,07	20,81	33,19	7,932	-	-	42,72	10,210	55,17	13,185
24	20 000	0,0028	75,04	17,935	89,62	21,42	-	-	-	-	-	-	-	-
25	50 000	0,0011	75,08	17,944	92,34	22,07	33,27	7,951	-	-	42,80	10,230	55,25	13,204
26	∞	1/∞	75,14	17,960	96,19	22,99	33,34	7,968	34,64	8,28	42,87	10,245	55,31	13,220

Molekulalarning tebranma harakat takrorligi chastotasi va yadrolararo masofa (r)

№	Molekula	Tebranish chastotasi sm^{-1}	Yadrolar oralig'i $r, \text{\AA}^0$	№	Molekula	Tebranish chastotasi sm^{-1}	Yadrolar oralig'i $r, \text{\AA}^0$
1	AgH^+	1760,0	1,617	14	$(^9\text{BeH}^-)^+$	2221,7	1,3122
2	$^{27}\text{Al}^{79}\text{Br}$	878,0	2,295	15	$(^9\text{BeH})^+$	1647,6	1,3114
3	$^{27}\text{Al}^{81}\text{Br}$	376,8	2,295	16	$^9\text{Be}^{16}\text{O}$	14,87,32	1,3308
4	$^{27}\text{Al}^{35}\text{Cl}$	481,30	2,14	17	$^9\text{Br}^{19}\text{F}$	673	1,7555
5	$^{27}\text{Al}^1/\text{H}$	1682,57	1,6456	18	$^{12}\text{C}^{16}\text{O}$	2170,21	1,1282
6	$^{27}\text{Al}^2\text{H}$	1212,02	1,5237	19	$^{12}\text{C}^{16}\text{O}$	2121,33	1,1291
7	$^{27}\text{Al}^{79}\text{Br}$	2305,04	1,5237	20	$^{12}\text{C}^{32}\text{S}$	1285,1	1,534
8	$^{197}\text{Au}^1/\text{H}$	1634,98	1,5239	21	^{12}CSe	1056,0	1,65
9	$^{11}\text{B}^{77}\text{Br}$	684,31	1,887	22	$^{40}\text{Ca}^{16}\text{O}$	732,1	1,822
10	$^{11}\text{B}^{35}\text{Cl}$	839,12	1,7157	23	$(\text{ClH})^+$	1775,4	1,667
11	$^{11}\text{B}^{19}\text{F}$	1400,6	1,267	24	$^{35}\text{Cl}^2$	564,9	1,993
12	$^{11}\text{B}^2\text{H}$	1780,0	1,231	25	$^{35}\text{Cl}^{19}\text{F}$	786,3	1,6281
13	$^9\text{Be}^{16}\text{O}$	669,8	1,940				

Ba'zi molekulalarning yadrolararo masofasi (r) va tebranma harakat chastotasi (m)

№	Molekula	Yadrolar oralig'i $r, \text{\AA}^0$	Tebranish chastotasi sm^{-1}	№	Molekula	Yadrolar oralig'i $r, \text{\AA}^0$	Tebranish chastotasi sm^{-1}
1	CO_2	1,162	2170,21	7	$^7\text{BeCl}_2$	1,7175	839,12
2	CS_2	1,534	1285,10	8	BH_3	1,231	1780,00
3	N_2O	1,125	1906,32	9	AlCl_3	2,14	483,30
4	SO_2	1,4321	1123,7	10	AlBr_3	2,196	376,80
5	NH_3	1,015	2030,00	11	Br_2	1,887	684,41
6	C_2H_2	1,1186	2811,60	12	HBr	1,231	1780,00

Ba'zi ionlarning cheksiz suyultirilgan eritmalaridagi ekvivalent elektr o'tkazuvchanligi (ionlar harakatchanligi)

Ion	λ_+	Ion	λ_-
Ag^+	61,9	OH^-	197,6
$\frac{1}{2} \text{Ba}^{2+}$	63,6	Br^-	78,14
$\frac{1}{2} \text{Ca}^{2+}$	39,6	Cl^-	76,35
$\frac{1}{2} \text{Cd}^{2+}$	64	ClO_3^-	04,6
$\frac{1}{2} \text{Cu}^{2+}$	53	ClO_4^-	67,3
$\frac{1}{2} \text{Fe}^{2+}$	53,5	$\frac{1}{2} \text{CO}_3^{2-}$	69,3
$\frac{1}{3} \text{Fe}^{3+}$	68	F^-	55,4
H^+	349,8	HCO_3^-	44,5
K^+	73,5	H_2PO_4^-	36
$\frac{1}{2} \text{Mg}^{2+}$	53,0	HSO_4^-	52
NH_4^+	73,7	$\frac{1}{2} \text{SO}_4^{2-}$	80,0
Na^+	50,1	NO_2^-	71,4
$\frac{1}{2} \text{Pb}^{2+}$	70	$\frac{1}{2} \text{S}^{2-}$	53,6
$\frac{1}{2} \text{Se}^{2+}$	59,5	$\frac{1}{2} \text{SO}_3^-$	72
$\frac{1}{2} \text{Zn}^{2+}$	54	HCOO^-	54,6
$\frac{1}{3} \text{Cr}^{3+}$	67	CH_3COO^-	49,9
		$\text{C}_6\text{H}_5\text{COO}^-$	32,3

25°C da suvdagi standart elektrod potentsiallari (π)

№	Elektrod	π^0 , V	№	Elektrod	π^0 , V
1	Cd^{2+} , Cd	- 0,403	6	Ag^+ , Ag	+ 0,799
2	Pb^{2+} , Pb	- 0,126	7	$\text{Cl}_2(\text{gaz})$, Cl	+ 0,136
3	H^+ , H_2	0,00	8	Ag, AgCl, Cl^-	+ 0,222
4	Cu^{2+} , Cu	+0,337	9	Ti^{3+} , Ti^{2+}	+ 1,25
5	Zn^{2+} , Zn	- 0,763	10	Kalomel KCl eritmasi 1) 0,1 n 2) 1,0 n 3) to'yingan	+ 0,337 + 0,282 1,2412

Kuchli elektrolitlarning 25°C dagi aktivlik koeffitsiyentlari ($\gamma_{\pm}$)

Elektrod	Konsentratsiya mol/100 g suvda													
	0,01	0,02	0,05	0,1	0,2	0,5	1,0	2,0	3,0	4,0	5,0	6,0	7,0	8,0
CuCl ₂	0,723	0,659	0,577	0,508	0,455	0,411	0,417	0,466	0,520	—	—	—	—	—
CuSO ₄	0,438	0,317	0,217	0,154	0,104	0,062	0,043	—	—	—	—	—	—	—
Cu(NO ₃) ₂	0,527	0,456	0,304	0,228	0,164	0,100	0,0669	0,0441	0,0352	—	—	—	—	—
CuSO ₄	0,399	0,307	0,206	0,150	0,102	0,061	0,041	0,032	0,033	—	—	—	—	—
CdJ ₂	0,379	0,0281	0,167	0,106	0,0685	0,0376	0,0251	0,0180	—	—	—	—	—	—
NaOH	0,905	0,871	0,818	0,766	0,727	0,690	0,678	0,700	0,784	0,903	1,077	1,299	1,03	2,01
HCl	0,904	0,875	0,830	0,795	0,767	0,757	0,809	1,000	1,316	1,762	2,38	3,22	4,37	—
HBr	0,906	0,870	0,838	0,805	0,768	0,790	0,871	1,183	1,603	—	—	—	—	—
H ₂ SO ₄	0,544	0,453	0,340	0,265	0,200	0,156	0,132	0,128	0,142	0,170	0,208	0,257	0,317	0,386
AgNO ₃	0,897	0,800	0,793	0,734	0,657	0,536	0,429	0,346	0,252	0,21	0,181	0,150	0,142	0,129
ZnSO ₄	0,387	0,298	0,202	0,150	0,104	0,063	0,043	0,035	0,041	—	—	—	—	—
FeCl ₂	0,75	0,70	0,02	0,52	0,47	0,45	0,51	0,70	—	—	—	—	—	—
TiClO ₄	—	—	—	0,730	0,652	0,527	—	—	—	—	—	—	—	—
Pb(NO ₃) ₂	0,69	0,60	0,40	0,37	0,27	0,17	0,11	—	—	—	—	—	—	—

MASALALAR JAVOBİ

I bob uchun

1. 3,6 kJ; 934 kJ 2. $2,12 \cdot 10^5$ Pa. 3. 12,5; 17,5 kJ. 4. 627 kJ. 5. 1,47 kJ. 6. 1,288. 7. 11,877 kJ/mol $\cdot$ grad. 8. 1921 kkal. 9. $C_p = 20,43 + 17,25 \cdot 10^{-31} T$. 10. 16,29 J; 389,5 kal. 11. 3806 kal. 12. 3,52 kJ; 25,3 km/m². 13. $a = 326$ kJ; $Q = 11,40$ kJ. 14. $1,0212 \cdot 10^4$ J. 15. $22,914 \cdot 10^4$ J. 16. 9027 kal. 17. -18530 kal; $-242,550$ kal; -224020 kal. 18. $Q = 402$ kal; $P_2 = 3,198$ atom. 19. 27,23 kJ. 20. 2,205; 1,420 0,726 kJ. 21. 38; 0384; 37,62 kJ. 22. 77°C ; $A = -389,4$ J; $\Delta U = 389,4$ J; $\Delta H = 546$ J.

II bob uchun

1. 126,2 kJ/mol. 2. -1884 kJ. 3. 86,0 kJ. 4. 1153,83 kJ. 6. 5 449 J/mol. 6. $-573,4 \cdot 10^6$ J. 7. $-34,918 \cdot 10^6$ J/kmol. 8. $-43,32$ kJ/mol; 9. $92179,4 \cdot 10^3$ J/mol. 10. $15 \cdot 53$ kal. 11. 288456 kkal/mol. 12. 44,10 kJ/mol. 13. 1) $-4,64$ kJ/g-atom. 2) $-13,9$ kJ/g-atom. 3) $0,7$ kJ/g-atom. 14. $-214,78$ kJ. 18. 82515 kal. 19. 84,82 kJ; 89,52 kJ. 20. 28,13 kJ. 21. 23117 kal/mol.

III bob uchun

1. 0,774 kJ/grad. 2. 15,19 J/grad. 3. 5,5 J/mol $\cdot$ grad. 4 172,70 J/mol $\cdot$ grad. 4. 177,70 J/mol $\cdot$ grad. 5. 31618 kJ/mol $\cdot$ grad. 6. 0,384 J/mol $\cdot$ grad. 7. 30,58 kJ/grad. 8. 3,166 kJ/g-atom $\cdot$ grad. 9. 100,34

J/mol · grad. **10.** 2 m³. **11.** 50,86 kal/mol · grad. **12.** 15,34 J/mol · grad. **13.** 230,6 J/grad. **14.** 23400 kal. **15.** 1993 kal; 2055 kal. **16.** 14348 kal. **17.** -122,52 J. **18.** 2492,8 J/g-atom. **19.-20.** Δ^0 — 21033 kal. $S_{580}^0 = 12,05$ kal/grad. **21.** -196993 kal. **22.** -510,2 J/mol. **23.** $A = -4476$ J; $\Delta U = 0$; $\Delta H = 0$ $\Delta S = 5,78$ J/mol · grad. $-\Delta F = \Delta G = -4470$ J/mol. **24.** $\Delta U = -409$ J/mol, $\Delta H = 652,5$ J/mol, $Q = 3820$ J/mol, $\Delta G = 362$ J/mol, $V = 3,7$ m³, $T = 188,6$ K.

IV bob uchun

1. 1,4; 4,84. **2.** 27,56. **3.** $3,44 \cdot 10^{-13}$ (N/m²); 14,3%. **4.** $13,92 \cdot 10^{-5}$ N/m². **5.** 0,932; 0,0352. **6.** 0,365; 5,768 mol/m³; $0,632 \cdot 10^4$ Pa. **7.** 0,617; 0,615. **8.** 0,563; 38. **9.** $4,1 \cdot 10^5$. **10.** 0,1923; 12,94%. **11.** 0,234. **12.** 0,661. **13.** 0,2. **14.** CO—1,44%; H₂O — 59,85%; CO₂ — 37,03%; H₂ — 1,68%. **15.** 0,721. **16.** $9,314 \cdot 10^{-3}$; 418,7; 238,5; 14,6 mm Hg. **17.** 48,49; -24,25; 27,25% (mol). **18.** 6,93702. **19.** 0,9255; 3,86 mol%; **20.** $57,54 \cdot 10^5$ N/m²; $4334 \cdot 10^5$ N/m². **22.** 0,31. **23.** 6,89%. **24.** 35,5%. **25.** ΔG : 190,8 kJ; 0; -44,53 kJ. **26.** 9,27 kJ; 0,142 kJ. **27.** 6,75 kJ; 0; -52 kJ. **28.** 5,35 kJ. **29.** 24,56 kJ; 0; -8,169 kJ. **30.** 21,48 kJ/mol. **31.** $1,986 \cdot 10^{-6}$. **32.** 627,3 K. **33.** -72,170 kJ. **34.** 219,33 kJ. **35.** 3,59; 41,84 kJ. **36.** 421,6 kJ/mol. **37.** 4454,08 m³/mol. **39.** $4,093 \cdot 10^{11}$; -273,96 kJ. **40.** $3,55 \cdot 10^{-6}$. **41.** 5,2518; NC₆H₆ = NC₂H₄(CH₃)₂ = 0,6217. **42.** $5,98 \cdot 10^5$. **43.** $2,723 \cdot 10^{33}$. **44.** 1,337. **45.** $1,718 \cdot 10^{-5}$. **46.** $K_p = 4,074 \cdot 10^{-3}$. **47.** $K_p = 1,274 \cdot 10^4$ atm² = $(1,27 \cdot 10^4 \cdot 1,003 \cdot 10^5)^2 = 1,31 \cdot 10^{14}$ N/m².

V bob uchun

1. $2,4993 \cdot 10^7$. 2. $1,1733 \cdot 10^2$. 3. 1,0117. 4. 2,5. 5. $5,9335 \cdot 10^{99}$. 6. $1,2025 \cdot 10^{10}$. 7. $5,5215 \cdot 10^{11}$. 8. $6,5424 \cdot 10^9$. 9. 12,4715 kJ/mol. 10. 8,3143 kJ/mol. 11. 2173 kJ/mol. 12. 22,959 kJ/mol. 13. $U = 3,7106$ kJ/mol. $S_{298} = 163,962$ J/mol · grad. 14. 48,1261 J/mol · grad. 15. $S_{298} = 0,0014$; $S_{1000} = 1,572$; $S_{3000} = 8,353$. 16. 210,884 J/mol · grad. 17. 12,4713 J/mol · grad. 19. 38. 819 J/mol · grad.

VI bob uchun

1. 0,733; 0,201; 0,066. 2. 4,909 mol/l; 4,909 g-ekv/l; 5,9 mol; 0,096. 3. 3,464 mol/l; 6,928 g-ekv/l; 3,861 mol; 0,065. 4. 0,4558; 0,388; 0,154. 5. 1,9 mol. 6. 1,134 mol; 0,02. 7. 20% 1,405 g-ekv/l; 1,468 mol; 0,026. 8. 9,63%; 2,773 mol/l; 5,546 g-ekv/l; 2,93 mol. 9. 1,391 mol; 1,345 mol/l; 0,0244. 10. 0,292 mol/l; 0,293 mol. 11. 8,732 mol/l; 15,31 mol/kg; 0,216. 12. 20%; 1,601 mol/l; 3,202 g-ekv/l; 0,029. 13. 2,795 mol/l; 8,385 g-ekv/l; 3,214 mol; $N_2 = 0,055$. 14. 6,05 mol/l; 0,123. 15. 3,038 mol/l; 3,352 mol/1000 g H_2O ; 20%; 0,057. 16. 48,84 sm^3/mol . 17. 502 sm^3 . 18. 39,72 sm^3/mol . 19. 20,44 sm^3/mol . 20. 27,3 sm^3/mol . 21. 23,7 sm^3 . 22. 8,75 sm^3/mol . 23. 18 sm^3/mol . 24. $\Delta G = -2972$ J; $\Delta S = 6,56$ J/grad. $\Delta H = -1017$ J. 25. 7,918 sm^3/mol . 26. 103,1 kJ. 27. 109,6 kJ. 28. 164,6 kJ. 28. 164,6 kJ. 29. 33760. 30. 357,3 kJ. 31. $-23,13 \cdot 10^3$ J ($-5,524$ kkal). 32. $-7,028 \cdot 10^3$ J ($-1,679$ kkal). 33. $-111 \cdot 10^3$ J ($-26,51$ kkal). 34. -7370 kal ($-7,370$ kkal). 35. -200 kal. 36. 5 kal. 37. 3790 kal. 38. -4900 kal. 39. 18550 kal. 40. $-0,149$; $-0,316$ kJ/mol. 41. $3,6 \cdot 10^3$ Pa.

42. 152 mm simob ustuni. **43.** 23,52 mm simob ustuni. **44.** 400,5 mm simob ustuni. **45.** 23,68 mm simob ustuni. **46.** 23,29 mm simob ustuni. **47.** $5,75 \cdot 10^4 \text{ N/m}^2$ (431,6 mm simob ustuni). **48.** 768,6 mm simob ustuni. **49.** 0,00036. **50.** 4,91%. **51.** 757 mm simob ustuni; 1,52%. **52.** 0,4213 g. **53.** 24,75 g. **54.** $-0,26^\circ\text{C}$. **55.** 1,86; 5,07; 7,81; 2,73 $\text{kmol}^{-1}\text{kg}$. **56.** 125,8 J/g. **57.** $-0,331^\circ\text{C}$. **58.** 110,3 J/g. **59.** 19,48 kJ/g-atom. **60.** 152,8. **61.** 0,077. **62.** 4,946 g. **63.** $561,3 \text{ n/m}^2$ (4,21 mm simob ustuni). **64.** 373,62 K; 3124 N/m^2 (23,43 mm simob ustuni). **65.** 87,64. **66.** 274,06 K. **67.** 34,4 kJ/mol. **68.** 16 kJ/mol. **69.** $80,44^\circ\text{C}$. **70.** 226,9. **71.** $100,06^\circ\text{C}$. **72.** 762,8 mm simob ustuni; $60,9^\circ\text{C}$. **73.** 757,3 mm simob ustuni; $100,102^\circ\text{C}$. **74.** 39,5 kJ/mol. **75.** 138,8. **76.** 373,18. **77.** 213,6. **78.** 8. **79.** 7394 kkal/mol. **80.** 365,0 J/g. **81.** $11,30^\circ\text{C}$. **82.** 2,67. **83.** 15,8. **84.** 789,5. **85.** $8,262 \cdot 10^{-3} \text{ mol/l}$. **86.** 9,187 mm simob ustuni; 0,1417m/l. **87.** $3,795 \text{ kg/m}^3$. **88.** $17,6 \cdot 10^{-4}$. **89.** 29,77. **90.** 0,0354. **91.** -38100 J/mol . **92.** 28677. J/mol. **93.** $-20348,15 \text{ J/mol}$. **94.** 73,6 g/l. **95.** 5,11 g. **96.** $80,36^\circ\text{C}$; 754,1 mm simob ustuni; 30,08 kal/g. **97.** 37,40 J/g-atom. **98.** -768 kJ . **99.** 0,3497 l. **100.** 0,0538 ml. **101.** 187 ml. **102.** $5,75 \cdot 10^{-5} \text{ g}$. **103.** 0,0898 g. **104.** 0,03. **105.** 27,74; 74,12. **106.** 1,3998; 23,3 $(\text{mol/l})^{-1}$. **107.** 1,21; 5,08; $7,64 \cdot 10^{-3}$. **108.** 1,53; 0,27 $(\text{mol/l})^{-1}$. **109.** $3 \cdot 10^{-4} \text{ mol/l}$. **110.** 17,74 g. **111.** $0,285 \text{ m}^3$. **112.** 0,474; 0,586; 0,715; 1,0; 0,468; 0,56; 0,687; 1,0; 0,458; 0,548; 0,681; 1,0. **113.** 0,86. **114.** 35,46. **115.** 1,864. **116.** 0,0975 l. **117.** 43 atm; 230 atm. **118.** 0,921. **119.** 1,16. **120.** 0,248; 0,83. **121.** 0,934. **122.** 6,60; 1,32. **123.** 0,966. **124.** 0,02448; 0,83. **125.** 0,583; 0,247; 0,911; 0,686.

VII bob uchun

1. 501,243 kJ/kg-atom; 2. 938,053 J/mol; 3. 0,0347 grad/mm; 4. 35,6 sm³/sek². 5. Na^{uz} = 0,248. 6. 0,563 kg; 7. 0,606 kg. 8. $1,947 \cdot 10^7$ N/m² (192,2 atm). 9. 245 kJ (58,52 kkal). 15. $P_2 = 0,7509 \cdot 10$ Pa. 16. 50,43 K. 17. $\Delta H_b = 38627,4$ J/kmol. 18. $\Delta H = 37,505 \cdot 10^6$. 19. 623,84 Pa. 20. 430 K. 25. $3,38 \cdot 10^4$; $4,24 \cdot 10^4$ N/m². 26. 0,765; 0,710; 0,696; 0,682 mol %. 27. $g_{\text{H}_2\text{O}} = 0,555$ kg; $T = 372,35$ K. 28. 0,43 va 0,85 mol %. 29. 1507⁰, 5196 Ni. Suyuq fazada 0,0277 kg, qattiq fazada 0,0443 kg; 1435⁰; 113% Ni. 30. 0,324 kg KCl.

VIII bob uchun

1. 0,7436. 2. 270. 3. 0,140 mol/l. 4. 3,14. 5. 3. 6. 21,4 g. 7. $5,15 \cdot 10^{-3}$. 8. 1,067. 9. $5,5 \cdot 10^{-5}$; $1,48 \cdot 10^{-5}$; $7,1 \cdot 10^{-3}$ $1,1 \cdot 10^{-3}$, $2,21 \cdot 10^{-7}$. $1,73 \cdot 10^{-5}$; $2,24 \cdot 10^{-5}$; $2,24 \cdot 10^{-4}$. $7,1 \cdot 10^{-5}$; $2,24 \cdot 10^{-4}$, $7,110^{-5}$; $1,73 \cdot 10^{-6}$; $8,5 \cdot 10^{-5}$ kmol/m³. 10. 0,082; 0,082; 0,039; 0,079. 11. 2,77%. 12. $C_{n+} = C_{\text{OH}^-} = 0,76 \cdot 10^{11}$ mol/l. 13. 0,54. 14. 6,7; 2,7; 1,68; 0,3; 0,087; 0,0721; 0,164; 0,27; 0,122. 15. $a_{\pm} = 0,077$; $a = 2,17 \cdot 10^{16}$ $a_{\text{Cr}^{3+}} = 0,0137$; $a_{\text{SO}_4^{2-}} = 0,0092$. 16. 0,011. 17. 0,888; 0,963. 18. 0,56; 0,84; 1,09. 19. 0,885; 0,845. 20. $2 \cdot 10^{-5}$. 21. $1,75 \cdot 10^{-5}$. 22. 2,76; 270. 23. 10,62. 24. $[\text{H}^+] = 5,58 \cdot 10^{-3}$; pH = 4,24. 26. $a = 0,28$; pH = 4,34. 27. $[\text{H}^+] = 0,76 \cdot 10^{-11}$ $[\text{OH}^-] = 1,33 \cdot 10^{-3}$; pH = 11,12. 28. $[\text{OH}^-] = 1,77 \cdot 10^{-6}$. 29. $J = 0,015$; $\gamma_{\pm} = 0,059$; $\gamma_{+, \text{H}^+} = 0,905$; pH = 2,19. 30. $a_{\text{Na}_2\text{SO}_4} = 3,04 \cdot 10^{-4}$; $a_{\text{HCl}} = 6,36 \cdot 10^{-3}$; $a_{\text{Pb}(\text{NO}_3)_2} = 1,01 \cdot 10^{-4}$. 31. $I = 0,14$; $\gamma_{\pm_{\text{Na}}} = 0,827$; $\gamma_{\pm_{\text{La}^{3+}}} = 0,25$;

$\gamma_{\text{Mg}^{2+}}^{\pm} = 0,403$; $\gamma_{\text{SO}_4^{2-}}^{\pm} = 0,32$; $\gamma_{\pm, \text{Cl}^-} = 0,826$. **32.** $K_p = 1,28 \cdot 10^{-4}$; $b = 1,67 \cdot 10^{-2}$. **33.** $1,13 \cdot 10^{-15}$. **34.** 2,078. **35.** 0,0049 mol/l. **36.** $6,28 \cdot 10^{-6}$ mol/l. **37.** $5,65 \cdot 10^{-4}$ mol/l; $1,88 \cdot 10^{-4}$ mol/l; $1,88 \cdot 10^{-4}$ mol/l. **38.** $1,21 \cdot 10^{-3}$; $2,33 \cdot 10^{-4}$ mol/l. **39.** $1,73 \cdot 10^{-10}$. **40.** $5 \cdot 10^{-13}$. **41.** $1,374 \cdot \Omega^{-1} \cdot \text{sm}^{-1}$. **42.** $\lambda_e = 7,61 \cdot 10^{-3} \Omega^{-1} \cdot \text{sm}^{-1}$; $\lambda_e = 38 \Omega^{-1} \cdot \text{sm}^2$. **43.** $3,7271 \cdot 10^{-3} \Omega^{-1} \cdot \text{sm}^{-1}$. **44.** $[\text{H}^+] = 1,3 \cdot 10^{-3}$ ion/l; $\lambda_e = 5,08 \Omega^{-1} \cdot \text{sm}^{-2}$ g-ekv $^{-1}$. **45.** $392,2 \Omega^{-1} \cdot \text{sm}^2$. **46.** $\lambda_e = 0,936 \cdot \Omega^{-1} \cdot \text{m}^2 / \text{kg-ekv} \cdot \lambda_m = 1,872 \Omega^{-1} \cdot \text{m}^2 / \text{kg} \cdot \text{mol}$. **47.** $30,39 \Omega^{-1} \cdot \text{sm}^2$ g-ekv $^{-1}$; $n = 0,292$. **48.** 65,57; 64,53. **49.** $\lambda_e = 0,55 \cdot 10^4$ $[\text{H}^+] = 6,5 \cdot 10^{-9}$. **50.** $10,4 \Omega^{-1} \cdot \text{sm}^2$. **51.** $\lambda_+ = 5,018$; $\lambda_- = 6,562 \Omega^{-1} \cdot \text{m}^2$; = 11,58. $n_{\text{Si}^{2+}} = 0,428$; $n_{\text{Cl}^-} = 0,572$. **52.** $\lambda_{\text{K}^+} = 6,06 \Omega^{-1} \cdot \text{m}^2$. $\lambda_{\text{ClO}_4^-} = 5,907 \Omega^{-1} \cdot \text{m}^2$. **53.** $n_+ = 0,4854$; $n = 0,5146$. **54.** $n_{\text{Cd}} = 0,430$; $n_{\text{Cl}^-} = 0,570$. **55.** $38,8 \Omega^{-1} \cdot \text{m}^2$. **56.** $K_D = 1,75 \cdot 10^{-5}$; pH = 4,319.

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3. 1,11 V. **4.** 0,9826. **5.** $1,38 \cdot 10^{-12}$. **6.** 1,041 · 7. 0,036 V. **8.** -0,3391. **9.** 0,902 V. **10.** $1,95 \cdot 10^{24}$. **11.** 10^{37} . **12.** 10^{56} . **16.** 2,78. **17.** -0,0096,6. **18.** 0,6404. **19.** $1,8 \cdot 10^{-10}$. **20.** $11 \cdot 10^{-7}$; $7 \cdot 10^{-7}$. **21.** $1,514 \cdot 10^{-3}$ mol/l. **22.** 0,0842. **23.** 0,31. **24.** 50175 kal. **25.** 15262 kal. -22,13 kal/grad. **26.** -460 -592 kJ/mol; -109,7 J/mol · grad. -594; -655 kJ/mol; -103,5 J/mol · grad. **27.** -1049 kal. **29.** 10142 kal.

X bob uchun

1. 2,33 A. 2. 0,28852. 3. 6,35 A. 4. 2,0373 ekv. 5. 0,1031 ekv. 6. 4,743 g; 9,480 g. 7. 12 minut 51 sek. 8. $6,34 \cdot 10^9$ J. 9. $5,6 \text{ sm}^3 \text{ O}_2$; $31,77 \text{ m}^2 \text{ Cu}$; $126,9 \text{ m}^2 \text{ J}_2$; $11,2 \text{ sm}^3 \text{ H}_2$. 10. 00268 A. 11. 92,7%; 12. 21,96 g-0,9248 l. 13. $0,2985 \cdot 0,1866 \text{ g-ekv/l}$. 14. 8 soat 13 minut, 9 soat 8 min. 15. $1,776 \cdot 10^3 \text{ sm}$. 16. 15,82.

XI bob uchun

1. $5 \cdot 10^{-4} \text{ sek}^{-1}$. $1,38 \cdot 10^{-3} \text{ sek}$. 2. $6,7 \text{ m}^3/\text{mol} \cdot \text{sek}$. 3. $0,515 \text{ min}^{-1}$. 4. $3,06 \cdot 10^{-5} \text{ sek}^{-1}$. 5. $0,103 \text{ min}^{-1}$. 1. 6. 7. 1,24 soat. —1. 8. $2,65 \cdot 10^{-4} \text{ min}^{-1}$, 1530 min. 9. $0,17 \text{ sek}^{-1}$. 1. 10. 2. 11. 0,0304 sek. 12. $2,7 \cdot 10^{-3} \text{ min}^{-1}$. 13. 30 min. 14. $K = 2,19-6 \text{ min}$ 2. 15. 7,544; 23,8; 238, 5 soat. 16. 740; 370 sek. 17. 51,5%. 18. $0,0925 \text{ kmol/m}^3$. 19. $0,86 \text{ mol}^{-1} \text{ min}^{-1}$. 20. 7,53 min. 21. 0,75 soat. 22. $4,24 \cdot 10^{-4}$; 1; 3720 sek. 23. 1. 24. 1. 25. $0,0123 \text{ min}^{-1}$; 1. 26. $1,7 \cdot 10^{-4} \text{ m}^3/\text{mol}$; 2. 27. 28. 1,40. 29. Ikkala modda bo'yicha 1. 30. 3. 31. $0,04 \cdot 10^{-1} \text{ soat}$. 1. 32. $4,19 \cdot 10^{-4} \text{ min}$; 1. 33. $5,31 \cdot 10^{-1} \text{ min}^{-1} \text{ g-ekv}^{-1}$; 1. 34. 3. 35. $2,35 \text{ min}^{-1} \cdot \text{g-ekv}^{-1}$; 1. 36. $11,6 \text{ min}^{-1} \text{ g-ekv}^{-1}$ l. 2. 37. $1,5 \cdot 10^{-3} \text{ sek}^{-1}$. 1,460 sek. 38. 4,41. 42. $k_1 = 0,032$; $k_2 = 0,032$; $k = 2,7$. 43. $k_1 = 2,48 \cdot 10^{-4} \text{ sek}^{-1}$ $k_2 = 1,79 \cdot 10^{-4} \text{ sek}^{-1}$. 45. $1,84 \cdot 10^{-3} \text{ min}^{-1}$. 46. 0,0326; 0,0074 kmol/m^2 . 47. 0,364 sek. 48. $k_1 = 0,356 \text{ min}^{-1}$ $k_2 = 5,72 \cdot 10^{-3}$. 49. $k_1 = 0,2 \text{ sek}^{-1}$; $k_2 = 1,0 \text{ m}^3/\text{kmol} \cdot \text{sek}$. 50. $k_1 = 238 \text{ min}^{-1}$, $k_2 = -1,25 \text{ min}^{-1}$. 51. $k_1 = 3,38 \cdot 10^{-3} \text{ sek}^{-1}$; $k_2 = 15,3 \cdot 10^{-3} \text{ sek}^{-1}$. 52. 25 kun. 52. 1,7. 53. 25 K. 54. 65 min. 55. 1,88; $k_1 = 0,069$; $k_2 = 457 \text{ min}^{-1}$. 56. 303 K. 57. $k_2 83,2 = 7,05 \cdot 10^{-3}$; $k_3 = 29 \cdot 10^{-3} \text{ l} \cdot \text{mol} \cdot \text{sek}^{-1}$. 58. 96,5 kJ/mol ; 59. 5,86. 60. 17,5 kJ/

mol. **61.** a) 12,5 kkal/mol (51,4 kJ/mol); b) 19,9 kkal/mol (83,3 kJ/mol); d) 29,1 kkal/mol (122 kJ/mol). **62.** $E = 86 \cdot 10^3$ J/mol; 1330 min. **63.** $12 \cdot 10$ sek. **64.** $k_3 = 3,16 \cdot 10^{-2}$ min. **65.** 107 marotaba. **66.** 8 kJ/mol. **67.** 35%. **68.** $E = 712$ J/mol. $k_0 = 0,0257$. **69.** $E = 210$ kJ/mol, 252 kJ/mol; $k_6 = 10 \cdot 12,35$; $k_{2,2} = 10^{12,54}$; $k_1 = 10^{12,35} e^{210/RT}$; $k_2 = 10^{12,54} e^{212/RT}$. **70.** $k_1 = 33,210 - \frac{23045,6}{T}$; $k_2 = 34,343 - \frac{21068,8}{T}$; 353 K da $k = 1,173 \cdot 10^{-2}$; 763 K da $k = 2,182 \cdot 10^{-2}$. **71.** $E = 12803,04$ J/mol. **72.** $7,8 \cdot 10^{-9}$ sek $^{-1}$. **73.** 3994 kJ/mol. **74.** $E = 4618,96$ J/mol; $P = 5,3 \cdot 10^{-10}$. **75.** $E = 54475,68$ J/mol. $P = 5,3 \cdot 10^{-8}$. **76.** $\Delta H^\# = 16,4$ kJ/mol; $\Delta S^\# = 37$ e. s. **77.** $\Delta H^\# = 13,2$ e; $\Delta S^\# = 21,8$ e. s. **78.** $\Delta F^\# = 17,15$ kJ/mol. **79.** 152,9. **80.** $7 \cdot 10^{-3}$ soat $^{-1}$. **81.** $\Delta H^\# = 72,147$ J/mol. $E = 74709,3$ J/mol. **82.** $\Delta H^\# = 121,330$ kJ/mol, $E = 233467$ J/mol. **83.** $\Delta H^\# = 124683$ J/mol. $\Delta S^\# = 39,33$ J/mol $\cdot$ grad. **84.** $E = 86,5$ kkal/mol ($3,12 \cdot 10^5$ J/mol); $\Delta H^\# = 85,9$ kkal/mol ($3,60 \cdot 10^5$ J/mol); $\Delta S^\# = 76$ e. s. ($1,76 \cdot 10^{-3}$ J/mol). **85.** $\Delta H^\# = 74,1 \cdot 10^{-5}$ J/mol (17,7 kkal/mol); $\Delta S^\# = -2,08 \cdot 10^{-6}$ /mol (20,8 e. s.). **86.** 55,38%. **87.** 103. **88.** 281,9 kJ/mol. **89.** $k_1 = 3,13 \cdot 10^{-7}$ sek, $k_2 = 9,35 \cdot 10^{-3}$, $E = 287,7$ kJ/mol. $E_{\text{el.mol}} = 191,196$. **90.** $E = 103,6$ kJ/mol, $E_{\text{el.mag}} = 471,03$ kJ/mol. **91.** $V = k_2 k_1 / 2 k_3$ Cl $\frac{3}{2}$. **92.** $V = k_2 (k_0 / k_3) [\text{C}_2\text{H}_4\text{Cl}]$. **93.** 24,6 kJ/mol. **94.** 254,7 kJ/mol.

XII bob uchun

1. $k_6 = 2,72 \cdot 10^2 \text{ m}$; $\text{pK} = 1,57$. 3. $k_0 = 1,34 \cdot 10^{-4}$. $K_{\text{OH}^-} = 5 \cdot 10^{-5} \text{ min}$. 6. 1,585. 9. $k_{\text{n}+} = 32 \text{ mol}^{-1} \cdot \text{sek}^{-1}$. 10. 2,72 marta. 11. $\Delta H_W^\# = 163 \text{ kJ}$, $\Delta H_{\text{Fe}}^\# = 200,9 \text{ kJ}$, $\Delta H_{\text{O}_2}^\# = 129 \text{ kJ}$. 13. $k_{\text{kat}} = 0,32 \text{ sek}^{-1}$, $k_m = 1,41 \cdot 10^{-2} \text{ m}$. 14. $k_{\text{kat}} = 5,08 \text{ sek}^{-1}$. $k_m = 1,42 \cdot 10^{-2} \text{ m}$. 15. $k_{\text{kat}} = 57,3 \text{ sek}^{-1}$. $k_m = 2,96 \cdot 10^{-4}$. 16. $k_{\text{kat}} = 66,5 \text{ sek}^{-1}$. $k_m = 2,13 \cdot 10^{-3} \text{ m}$. 17. $k_m = 2,13 \cdot 10^{-3} \text{ m}$. 18. $k_{\text{kat}} = 6,53 \text{ sek}^{-1}$. $k_m = 1,83 \cdot 10^{-2} \text{ m}$.

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