O‘zbekiston Respublikasi Sog‘liqni saqlash vazirligi
TOSHKENT FARMATSEVTIKA INSTITUTI
NOORGANIK, FIZIK VA KOLLOID KIMYO KAFEDRASI

1-MA’RUZA:

KIMYOVIY REAKSIYALAR ENERGETIKASI

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TOSHKENT-2022

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1-ma’ruza: Kimyoviy reaksiyalar energetikasi

REJA:

Mavzuning ma’ruza davomida yoritiladigan qismlari:

1. Ichki energiya;
2. Gess qonuni;
3. Termokimyoviy hisoblar;
4. Entalpiya;
5. Entropiya;
6. Izobar-izotermik va izoxor-izotermik potensiallar;
7. Kimyoviy reaksiyalar yo’nalishini aniqlash;

Mavzuning talaba mustaqil o’zlashtirishi lozim bo’lgan qismlari:

Kimyoning asosiy qonunlari:

1. **Moddalar massasi saqlanish qonuni;**
2. **Tarkibning doimiylik qonuni;**
3. **Karrali nisbatlar qonuni;**
4. **Hajmiy nisbatlar qonuni;**
5. **Gaz qonunlari *(Boyl-Marroit, Gey-Lyussak u Sharl qonunlari);***
6. **Avogadro qonuni;**
7. **Ekvivalentlar qonuni.**

Termokimyoviy tenglamalarning o’ziga xosligi:

1. Tenglamalar tizim holatining TD funksiyalarini (ΔH, ΔS) hisobga olgan holda yoziladi.

2. Tenglamalarda 1 mol modda hisobga olinadi, shuning uchun kasr ko’rinishidagi koeffitsientlardan foydalanish mumkin.

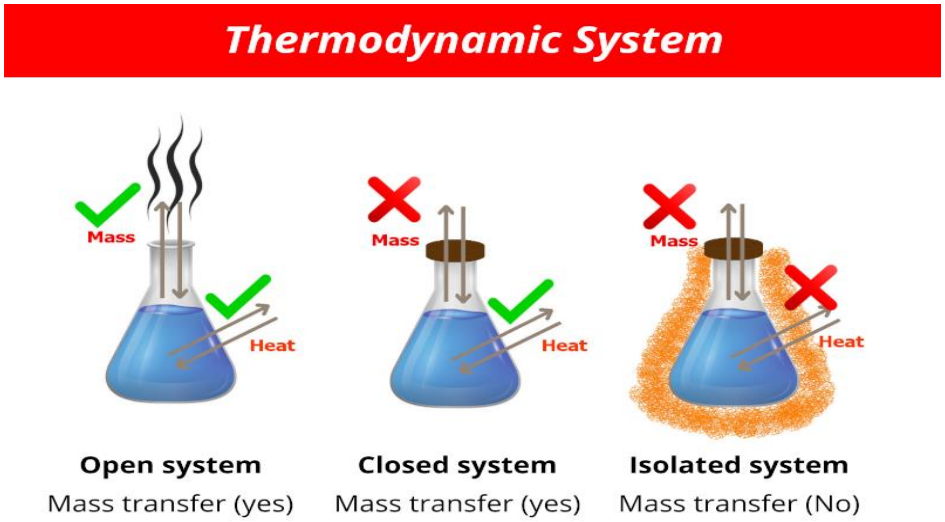
3. Moddalarning agregat holati ko’rsatiladi.

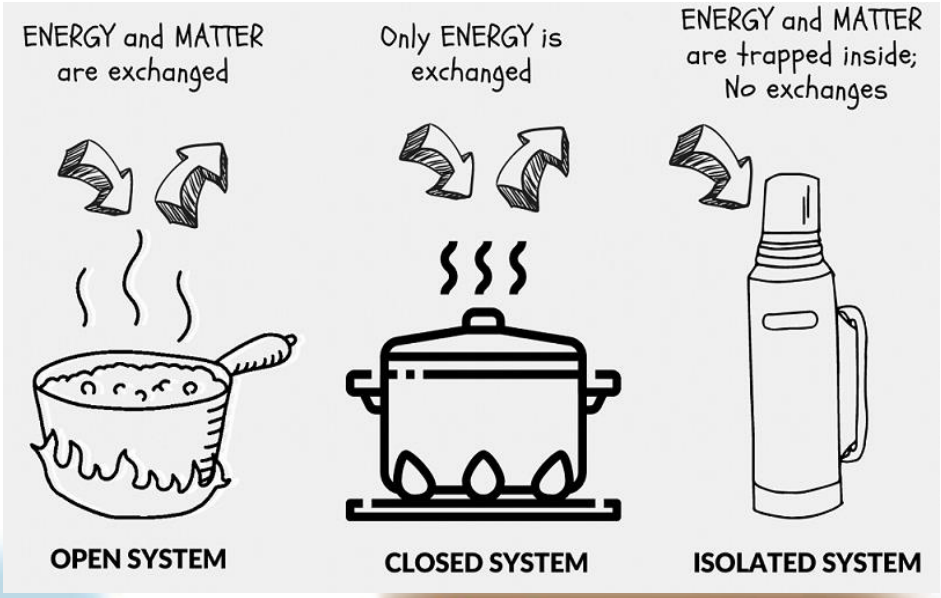
4. TK tenglamalar bilan oddiy algebraik amallarni bajarish mumkin.

Masalan: $\frac{1}{2}\ N_{2(g)} + \frac{1}{2}\ O_{2(g)} = NO_{(g)}$, $\Delta H > 0$.

Tizim - bu atrof-muhitdan real va hayoliy jihatdan ajratilgan jism yoki o'zaro ta'sir qiluvchi (diffuziya, issiqlik almashinuvi, kimyoviy reaksiya) jismlar to'plamidir.

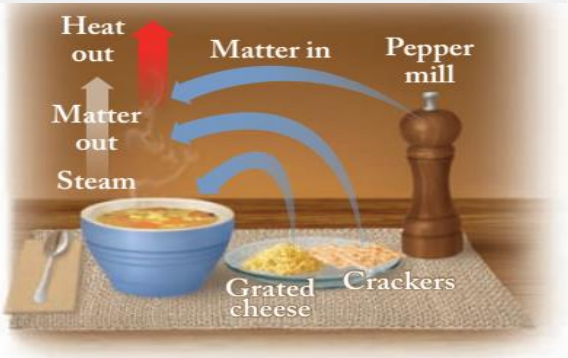
Atrof-muhit - bu tizim bilan bevosita yoki bilvosita aloqada bo'lgan barcha narsa.





(a) **Isolated system:** A thermos bottle containing hot soup with the lid screwed on tightly

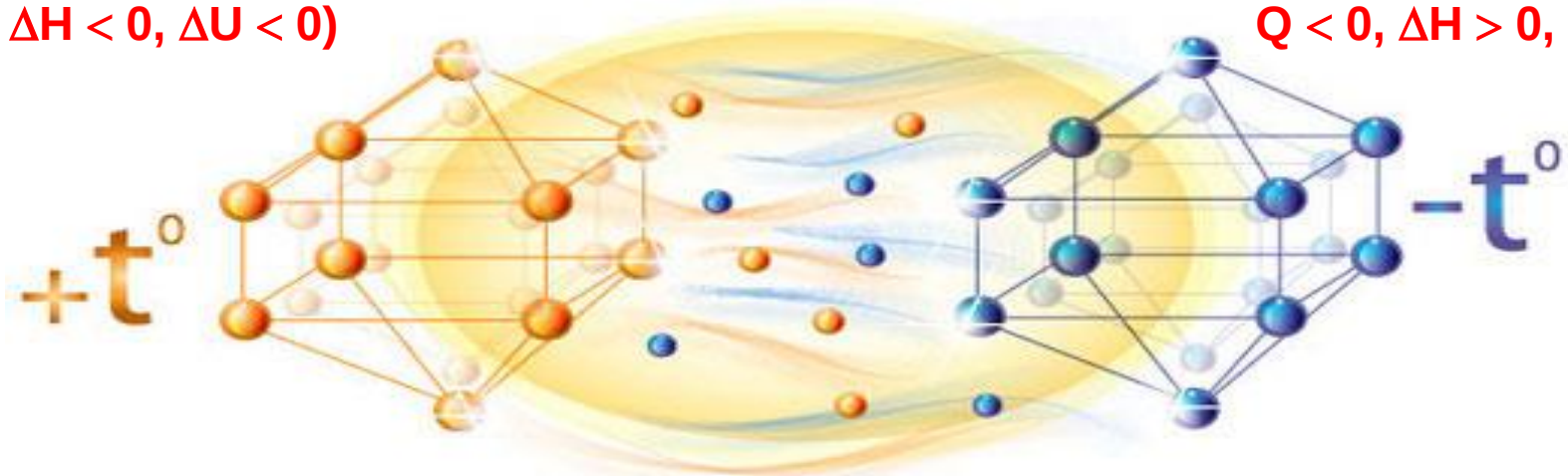
(b) **Closed system:** A cup of hot soup with a lid



(c) **Open system:** An open cup of hot soup

Barcha kimyoviy jarayonlar - issiqlik (energiya) ajralishi yoki yutilishi bilan birga kechadi.

(Q > 0, ΔH < 0, ΔU < 0) **Q < 0, ΔH > 0, ΔU > 0)**



Termokimyoviy reaksiyalar

Reaksiya jarayonida ajralib chiqadigan yoki yutilgan issiqlik miqdori – ***issiqlik effekti*** deb nomlanadi.

Kimyoviy reaksiyalarning issiqlik effekti reaksiyaga kirishuvchi moddalarning tabiatiga va ularning agregat holatiga bog‘liq.

Issiqlik effektlari standart sharoitlarda (st.sh.) o'lchanadi.

St.sh. T 298 K (25°C) и 101,325 kPa. Termokimyoviy tenglamalar:

$2H_2$ (g) + O_2 (g) = $2H_2O$ (s) + 571,6 kj

H_2 (g) + $1/2O_2$ (g) = H_2O (s) + 285,3 kj

H_2 (g) + $1/2O_2$ (g) = H_2O (g) + 241 kj

N_2 (g) + O_2 (g) = 2NO (g) - 180,5 kj

$1/2N_2O$ (g) + $1/2O_2$ (g) = NO (s) - 90,25 kj

- Tizimning barcha fizikaviy va kimyoviy xossalarining yig'indisi *tizimning holati* deb ataladi.
- U ***termodinamik parametrlar*** bilan tavsiflanadi, ular:
- ***Intensiv*** - bular *massaga bog'liq bo'lmagan* va tizimlar bilan aloqa qilganda (harorat, bosim, zichlik, kontsentratsiya, kimyoviy potentsial) mos keladigan xususiyatlar.
- Sistemaning *massaga bog'liq bo'lgan* xossalari ***ekstensiv*** (hajm, massa, issiqlik sig'imi, ichki energiya, entalpiya, entropiya, termodinamik potensiallar) deyiladi.
- *Agar termodinamik parametrlardan kamida bittasi tizimda bir muncha vaqt o'zgarsa, bu* ***termodinamik jarayonning*** *paydo bo'lishini anglatadi:* **Izotermik (t = const); Izoxorik (V = const); Izobarik (p = const).**

Tizim holati funksiyalari

Tizimning termodinamik funksiyalariga quyidagilar kiradi:

1. **Ichki energiya (U).**
2. **Entalpiya (H).**
3. **Entropiya (S).**
4. **Gibbs energiyasi (erkin energiya) (G).**
5. **Gelmgols energiyasi (F).**

Ichki energiya (ΔU) **- bu tizimning ichki energiyasi, molekulalarning translatsiya va aylanish harakatlaridan, atomlar va atom guruhlarining molekula ichidagi tebranishlari energiyasidan, atomlardagi elektronlarning harakati energiyasidan, yadrolararo va yadro ichidagi energiyadan iborat bo'lgan umumiy energiya zahirasi hisoblanadi.** ***ΔU ni o'lchash mumkin emas, chunki materiyani harakatdan mahrum qilish mumkin emas.***

Atrof muhit bilan ***issiqlik almashinuvi*** **bo'lmasa, tizimning umumiy ichki energiyasi** ***o'zgarishsiz*** **qoladi.**

Tizimning bir holatdan ikkinchi holatga o'tishida, uning ichki energiyasining ΔU o'zgarishi – tashqi kuchlarga qarshi bajarilgan ish (A) va tizimga beriladigan issiqlik miqdoriga (Q) lar yig'indisiga teng: $\Delta U = A + Q$

Gess qonuni (1841 y.):

Reaksiyaning issiqlik effekti reaksiyada ishtirok etuvchi moddalarning boshlang'ich va oxirgi holatlarigagina bog'liq bo'lib, jarayonni qaysi usulda olib borishga (oraliq bosqichlarga) bog'liq emas.

1) $C_{(grafit)} + O_{2\ (g)} = CO_{2\ (g)}$ $\Delta H_1 = -396,0$ kj

2) $2C_{(garfit)} + 0,5O_2 = 2CO$ $\Delta H_2 = -110,5$ kj

3) $CO_{(g)} + 0,5O_2 = CO_2$ $\Delta H_3 = -285,5$ kj

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

ΔH_3 qiymatini Gess qonuniga asosan aniqlash m-n:

$$\Delta H_3 = \Delta H_1 - \Delta H_2 = -396,0 - (-110,5) = -285,5$$

$$\Delta H_2 = \Delta H_1 - \Delta H_3 = -396,0 - (-285,5) = -110,5$$

Kimyoviy jarayonlar sodir bo'ladi: (V=const; T=const yoki P=const).

Termodinamikaning birinchi qonuni: tizimga berilgan issiqlik miqdori tizimning tashqi kuchlarga qarshi ish bajarishiga va tizimning ichki energiyasini o'zgarishiga sarflanadi.

$$\Delta Q = (Q_2 - Q_1) = \Delta U + A \qquad \Delta U = U_2 - U_1$$

$$A = P\Delta V = P(V_2 - V_1)$$

$$Q_p = \Delta U + P(V_2 - V_1) = U_2 - U_1 + P(V_2 - V_1) =$$

$$= (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1$$

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

$$H = U + PV \quad \text{или} \quad \Delta H = \Delta U + P\Delta V$$

ΔH – entalqiya.

Entalpiya - bu tizimning kengayish energiyasi.

O'zgarmas bosimda (p=const) termodinamikaning birinchi qonuniga asosan, reaksiyaning issiqlik effekti entalpiya o'zgarishiga teng.

Agar jarayon doimiy hajmda sodir bo'lsa (V=const), u holda reaksiyaning issiqlik effekti ichki energiyaning o'zgarishiga teng bo'ladi:

$$Q_v = \Delta U + A = U_2 - U_1 + A \qquad A=0$$

$$Q_v = U_2 - U_1 = \Delta U \qquad Q_v = \Delta U$$

$$Q_p - Q_v = P\Delta V$$

Doimiy bosim va hajmdagi issiqlik effektlarning farqi gazning kengayish ishiga teng. $P\Delta V = \Delta nRT$

Δn – gaz holidagi reaksiya ishtirokchilari sonining o‘zgarishi (mollarda).

$$Q_p - Q_v = \Delta nRT \text{ yoki } \Delta H = \Delta U + \Delta nRT$$

Agar $\Delta n=0$, u holda $\Delta H=\Delta U$

Agar kimyoviy reaksiyalarda qattiq yoki suyuqliklar ishtirok etsa, u holda Δn *hisobga olinmaydi.*

Δn – reaksiya koeffitsientlarining stexiometrik o'zgarishi.

Suyuq suvning issiqlik effektini hisoblash:

298 K $Q_v = -284,2$ kj/mol = ΔU.

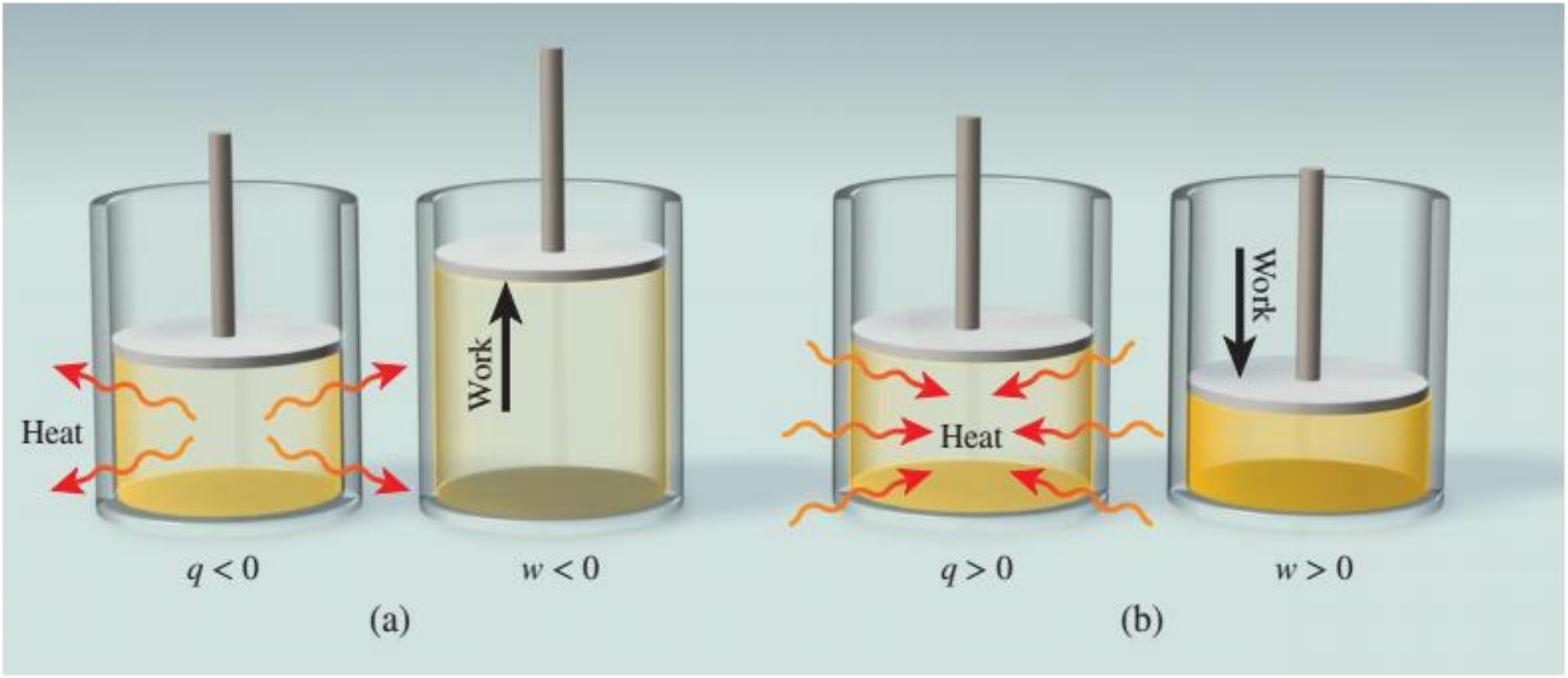
$$2H_2\,(g) + O_2\,(g) = 2H_2O\,(s)$$

$$\Delta n = \Sigma n_{\text{mahsulotlar}} - \Sigma n_{\text{dastlabki moddalar}} = 0 - 3 = -3$$

$$\Delta H = \Delta U + \Delta nRT = -284,2 - 3*8,314*298 = -284,2 - 7,4 = -291,6 \text{ kj/mol.}$$

TABLE 5.1 Sign Conventions for Heat (q) and Work (w)

Process	Sign
Heat absorbed by the system (endothermic process)	q is positive
Heat released by the system (exothermic process)	q is negative
Work done on the system by the surroundings (e.g., a volume decrease)	w is positive
Work done by the system on the surroundings (e.g., a volume increase)	w is negative



Termokimyoviy hisoblar

St. hosil bo'lish issiqligi **(entalpiya) deb, st.sh.da barqaror bo'lgan oddiy moddalardan 1 mol murakkab modda hosil bo'lishining issiqlik effekti tushuniladi. (masalan: grafit, rombik oltingugurt, oq fosfor, kristal. yod va h.k.).**

H.b. ($\Delta H^o_{f,\,298}$). f-inglizcha. "formation" – hosil bo'lish.

Oddiy moddalar uchun standart hosil bo'lish entalpiyasi = 0.

$$\Delta H^\circ h.b\ (oddiy\ moddalar) = 0$$

Yonish issiqligi **(entalpiya) deb, 1 mol moddaning mol miqdorda kislorod atmosferasida yuqori oksidlarigacha yonish issiqligi tushuniladi.**

H.b.($\Delta H^o_{c,\,298}$). inglizcha. "combation" – yonish

Oddiy moddalar hosil bo'lish standart entalpiyalari nolga teng (gaz O_2, suyuq Br_2, yod kristallari, romb. S, grafit).

$$H_{2\,(g)} + 1/2O_{2\,(g)} = H_2O_{\,(s)}$$

$$\Delta H^{o}_{f,\,298} = -285{,}3\ kj/mol$$

$$H_{2\,(g)} + 1/2O_{2\,(g)} = H_2O_{\,(g)}$$

$$\Delta H^{o}_{f,\,298} = -241{,}8\ kj/mol$$

Gess qonuniga asosan: Kimyoviy reaksiyaning hosil bo'lish issiqlik effektini (st.sh.) hisoblash uchun, reaksiya mahsulotlarining issiqlik effektlari yig'indisidan (reaksiya tenglamasida stexiometrik koeffitsientlarni hisobga olgan holda) boshlang'ich moddalarning issiqlik effektlari yig'indisi ayiriladi.

aA+bB=cC+dD

$$\Delta H^{o}_{reaksiya} = \sum n_{mah} \cdot \Delta H^{o}_{f,298\,mahsulotlar} - \sum n_{dast.\mathrm{mod.}} \cdot \Delta H^{o}_{f,298\,dast.\mathrm{mod}dalar}$$

Ba’zi moddalarning st. h. b. entalpiyalari ($\Delta H^o_{f,298}$) qiymati

Moddalar	$\Delta H^o_{f,298}$, kj/mol	Moddalar	$\Delta H^o_{f,298}$, kj/mol
Al (g)	326,3	H_2O (s)	-285,3
Al^{3+}(s)	-530	H_2SO_4 (s)	-814,2
Al_2O_3 (q)	-1676,0	K+ (s)	-251,2
$Al_2(SO_4)_3$	-3442,2	KCl (q)	-435,9
C (olmos)	1,828	$KClO_3$ (q)	-391,2
CH_4 (g)	-74,86	KNO_3 (q)	-493,2
CO (g)	-110,5	KOH (q)	-425,8
CO_2 (g)	-393,5	$MgSO_4$ (q)	-1301,4
$CaCO_3$ (q)	-1206,9	$MgSO_{4*}7H_2O$ (q)	-3384

Entalpiya kalloriyalarda o’lchanadi:

1 kall 1 g suvni 1 ^oC qizdiradi

yoki 1 kj 1 g suvni 0,24 ^oC ga qizdiradi

Masalan: $Al_2O_3\ (q) + 3SO_3\ (g) = Al_2(SO_4)_3\ (q)$

Reaksiyaning issiqlik effektini hisoblang:

$\Delta H^\circ_{f,298}\ Al_2O_3\ (q) = -1676,0$ kj/mol;

$\Delta H^\circ_{f,298}\ SO_3\ (g) = -396,1$ kj/mol;

$\Delta H^\circ_{f,298}\ Al_2(SO_4)_3 = -3442,2$ kj/mol.

$$\Delta H^\circ_{r\text{-}ya} = (\Delta H^\circ_{f,298}\ Al_2(SO_4)_3) - (\Delta H^\circ_{f,298}\ Al_2O_3 + 3\Delta H^\circ_{f,298}\ SO_3) =$$

$$-3442,2 - [-1676,0 + 3(-396,1)] = -577,9 \text{ kj/mol}$$

Reaksiyaning yonish issiqlik effektini hisoblash uchun dastlabki moddalarning yonish issiqlik effektlari yig'indisidan reaksiya mahsulotlarining yonish issiqlik effektlari yig'indisi ayiriladi.

$$\Delta H^\circ_{reaksiya} = \sum n_{dast.mod.} \cdot \Delta H^\circ_{C,298\,dast.mod.} - \sum n_{mah} \cdot \Delta H^\circ_{C,298\,mah.}$$

Neytrallanish issiqligi

$$2NaOH\ (s) + H_2SO_4\ (s) = Na_2SO_4\ (s) + 2H_2O$$

$$\Delta H^\circ_{neytr.} = -57,5 \text{ kj/mol}$$

1) Erish jarayoni:

$$KOH\ (q) + aq \rightarrow K^{+}(e\text{-}ma) + OH^{-}(e\text{-}ma)$$

$$-425,8 \qquad -251,2 \qquad -230,2$$

$$\Delta H^{o}\ erish = |(-251,2+(-230,2)| - (-425,8) = -55,6\ kj/mol$$

2) Qattiq (kristall) Na ning bug' (gaz) holatiga o'tishi:

$$Na\ (q) \rightarrow Na\ (g)$$

$$0 \qquad 108,3$$

$$\Delta H^{o}_{bug'lanish} = 108,3 - 0 = 108,3\ kj/mol$$

3) Dissotsiyalanish jarayoni, molekulaning atomlarga parchalanishi: $Cl_2\ (g) \rightarrow 2Cl\ (g)$

$$0 \qquad 2(121,3)$$

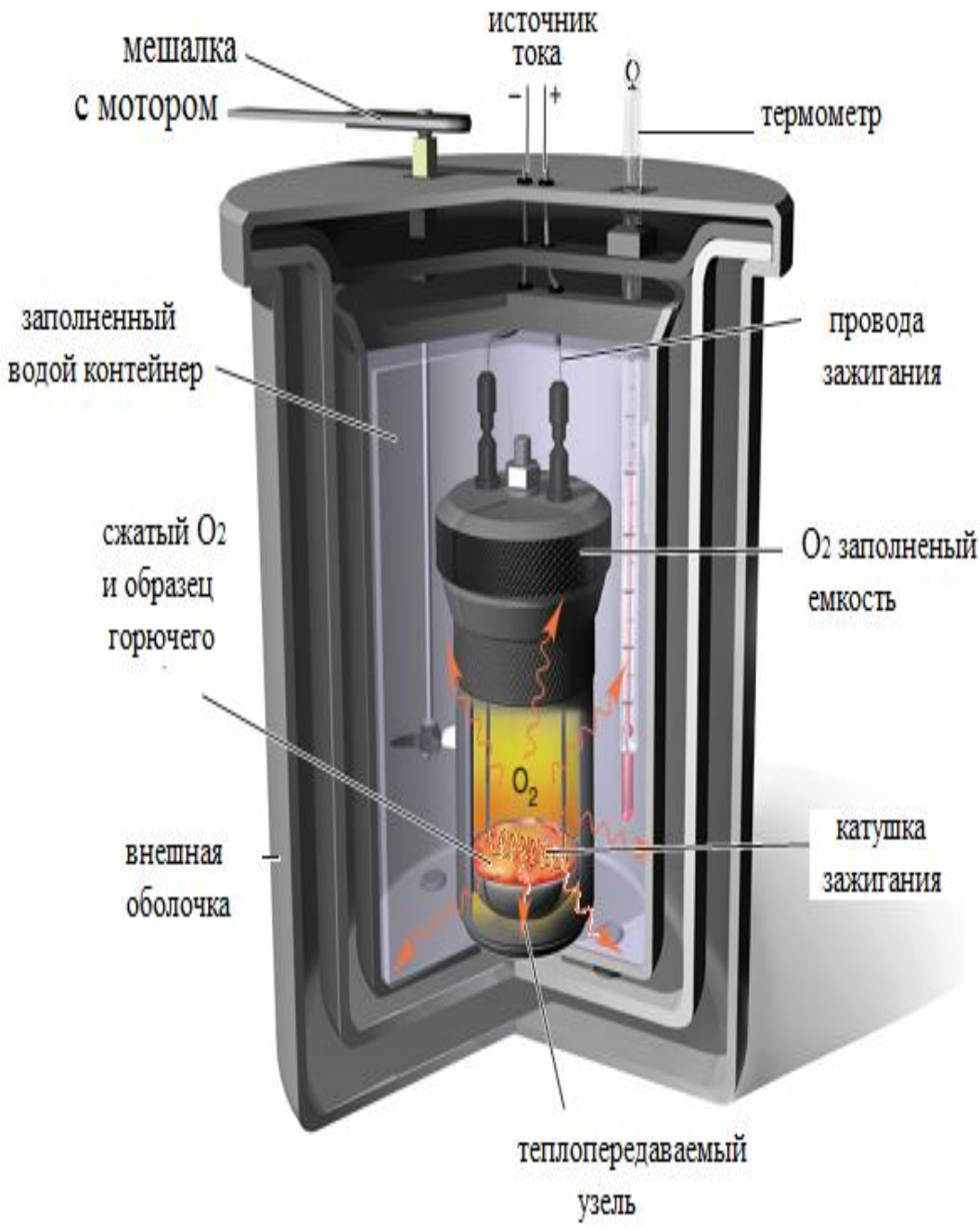
$$\Delta H^{o}_{diss} = 2(121,3) - 0 = 242,6\ kj/mol$$

4) Ionlanish jarayoni: $H\ (g) \rightarrow H^{+} + e^{-}$

$$217,98 \qquad 1536,2$$

$$\Delta H^{o}_{ionlanish} = 1536,2 - 217,98 = 1318,22\ kj/mol$$

Калориметр



Kalorimetr tuzilishi

$$\Delta H_m = \frac{\Delta h_1}{m_1 \cdot M_1}$$

$$\Delta h_i = Cк \cdot \Delta Ti$$

$$Cк = \sum Cp_i \cdot m_i$$

Ck kalorimetrik tizimning issiqlik sig'imi

KALORIMETRIK BOMBA

Kimyoviy reaksiyalar yo’nalishi

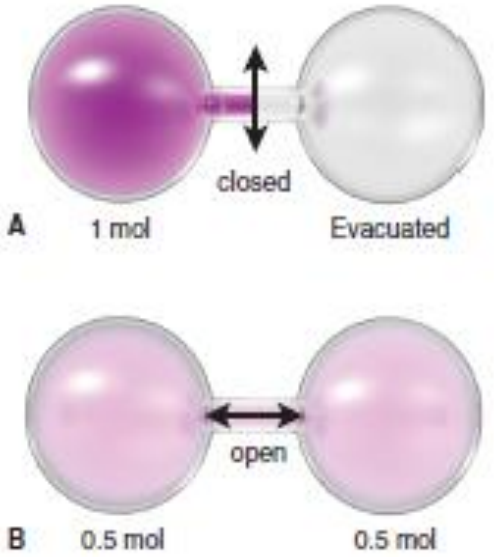
Entropiya. **Bu tizim tartibsizligi o'lchovidir. Entropiyani (S) o'lchash uchun Boltsman formulasidan foydalaniladi:**

$$S = k \ln W$$

$k = R/Na = 1{,}3806505(24)\cdot 10^{-23}$ j/k

k – Boltsman doimiysi.

W – bu holatning ehtimoli.



"Tabiat va undagi hodisalar kamroq ehtimoliy holatlardan, ko'proq ehtimoliy holatlarga intiladi.

$$S = R \ln \frac{\text{2- holatdagi tartibsizlik}}{\text{1 -holatdagi tartibsizlik}}$$

Entropiyaning mutlaq qiymatini aniqlash mumkin emas.

Biroq, bir holatdan ikkinchi holatga o'tishda entropiyaning o'zgarishini aniqlash mumkin.

O'lchov birligi S - J / mol * K

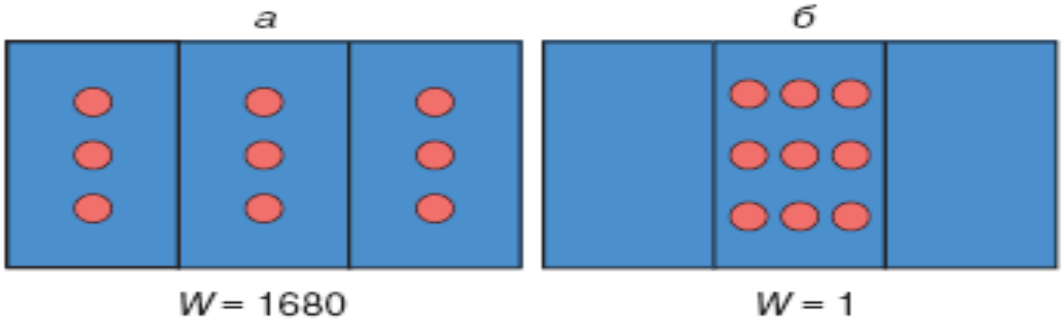
ΔS - issiqlik effekti o'zgarishining mutlaq haroratga nisbati:

$$\Delta S = \frac{\Delta Q}{T}$$

ΔQ – issqilik effektining o'zgarishi; T – absolyut harorat K; S o'lchov birligi j/mol K.

"Izolyatsiya qilingan (izolirlangan) tizimlarda faqat shunday jarayonlar o'z-o'zidan sodir bo'lishi mumkinki, bunda jarayon tizimning entropiyasi ortishi bilan kechadi"

Tizimning to'liq tartibsizlik (a) dan to'liq tartib (b) ga o'tishida termodinamik ehtimollik *W* o'zgaradi, demak, Plank-Boltsman tenglamasiga muvofiq *S=klnW* ga teng bo'lgan S entropiyasi o'zgaradi. Tizim qanchalik tartibli bo'lsa, uning entropiyasi shunchalik kamayadi.

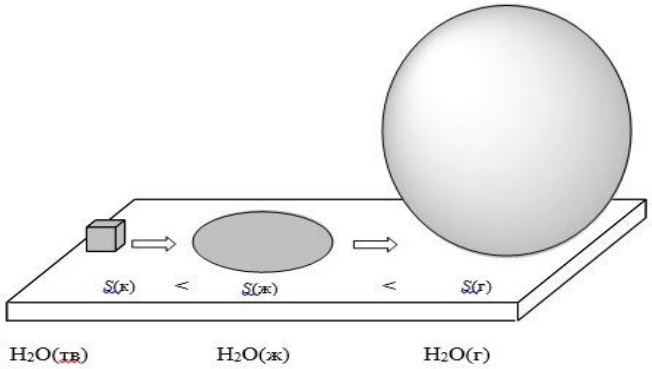


Masalan: 1 mol muz erishi entropiyasining o'zgarishini aniqlaymiz.

Q – muzning erish issiqligi, 6016,432 j/mol;

T = 273,15; ΔS = 6016,432/273,15 = 22 j/mol

1) Hajm ortishi bilan entropiya ham ortadi.



$C(q) + CO_2(g) = 2CO(g)$

1v 2v

ΔS_1 ΔS_2 $\Delta S_2 > \Delta S_1$ $\Delta S > 0$

2) $N_2 + 3H_2 = 2NH_3$ hajm kamayganda, S kamayadi.

1v 3v 2v $\Delta S < 0$

3) Hajm o'zgarmasa – entropiya o'zgarmaydi.

$H_2 + Cl_2 = 2HCl$

1v 1v 2v $\Delta S = 0$

Kimyoviy jarayonlarning o'z-o'zidan borishi:

1) **Tizim minimal energiyaga erishishga harakat qiladi.**
2) **Kichikroq zarrachalardan kattaroq zarrachalar hosil qilishga moyillik.**

Birikish jarayoni ekzotermik:

$2H_2 + O_2 = 2H_2O + Q$ ($\Delta H < 0$)

$CaO + H_2O = Ca(OH)_2 + Q$ ($\Delta H < 0$)

Katta zarralar parchalanganda entropiya qiymati ortadi:

$2NH_3 = N_2 + 3H_2$

2v 1v 3v

Tizimning entropiyasi o'zgarishi (ΔS) – mahsulotlar absolyut entropiyasi qiymati yig'indisidan, dastlabki moddalar absolyut entropiyasi qiymati yig'indisini ayirmasiga teng.

$$\Delta S^{o}_{reaksiya} = \sum n_{mah.} \cdot \Delta S^{o}_{298 mah.} - \sum n_{dast.\text{mod.}} \cdot \Delta S^{o}_{298\ dastl.\text{mod.}}$$

Ba’zi moddalarning standart entropiyalari (S^o_{298}) qiymati

Modda	S^o_{298}	Modda	S^o_{298}	Modda	S^o_{298}
Ag (q)	42,55	Fe (q)	60,29	NaCl (q)	72,36
AgBr (q)	107,1	FeO (q)	60,75	Na_2CO_3 (q)	136,4
AgCl (q)	96,07	Ge (q)	31,1	O (g)	160,95
AgI (q)	115,5	H+ (s)	O	O_2 (g)	205,04
Al (q)	28,35	H_2 (g)	130,52	O_3 (g)	238,8
$BaCO_3$ (q)	112	HNO_3 (s)	156,6	OH^- (s)	-10,88
$BaCl_2$ (q)	126	NH_3 (g)	192,6	P oq	41,1

Masalan: $N_{2\,(g)} + 3H_{2\,(g)} = 2NH_{3\,(g)}$

Hajm kamayganda, S qiymati kamayadi:

$\Delta S^{\circ}_{r} = 2(192,6) - [199,9+3(130,52)] = -206,26$ j/grad*mol

$C_{\,(grafit)} + CO_{2\,(g)} = 2CO_{\,(g)}$

S ortadi:

$\Delta S^{\circ}_{r} = 2(197,54) - (5,74+213,68) = 175,66$ j/grad*mol

Qattiq moddalar uchun S qiymati o'zgarishi sezilarsiz:

$Al_{\,(q)} + P_{\,(q)} = AlP_{\,(q)}$

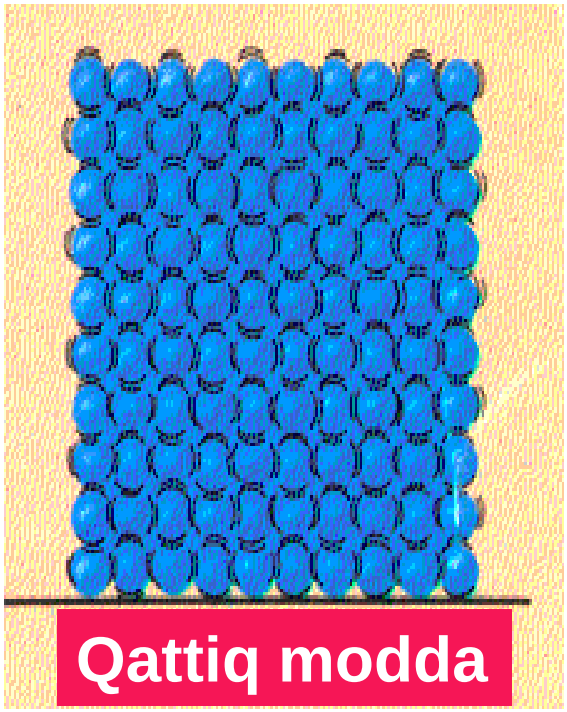
Suyuqliklarning bug' (gaz) ga o'tishi, kristalning erishi, qattiq moddalarning erishi bilan S ortadi.

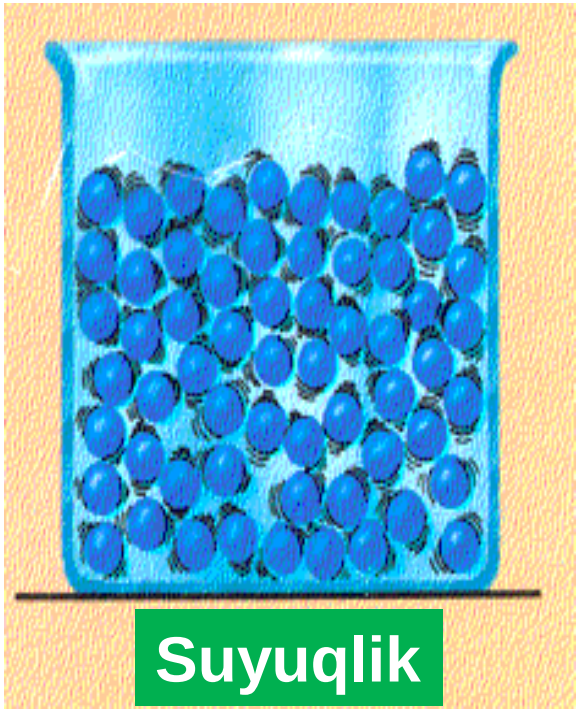
Bug' (gaz) larning kondensatsiyasi, suyuqliklarning kristallanishi va hajmining kamayishi bilan S kamayadi.

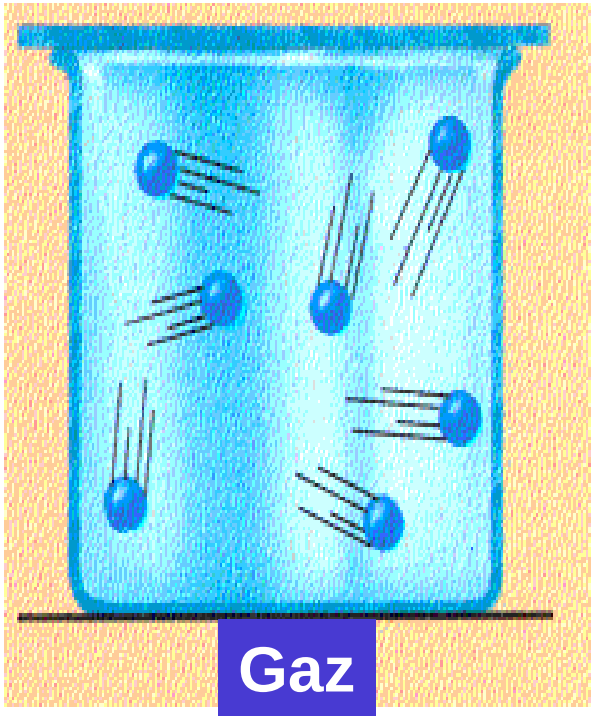
$H_2O_{\,(s)} \rightarrow H_2O_{\,(g)}$ $\Delta S^{\circ}r = 188,72-70,08 = 118,64$ j/grad*mol

70,08 188,72

Entropiya

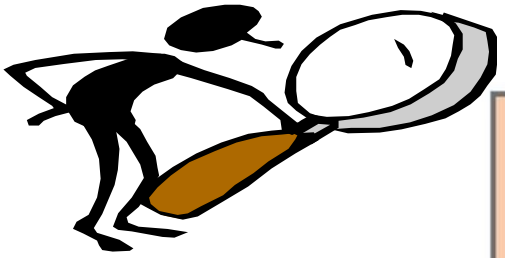




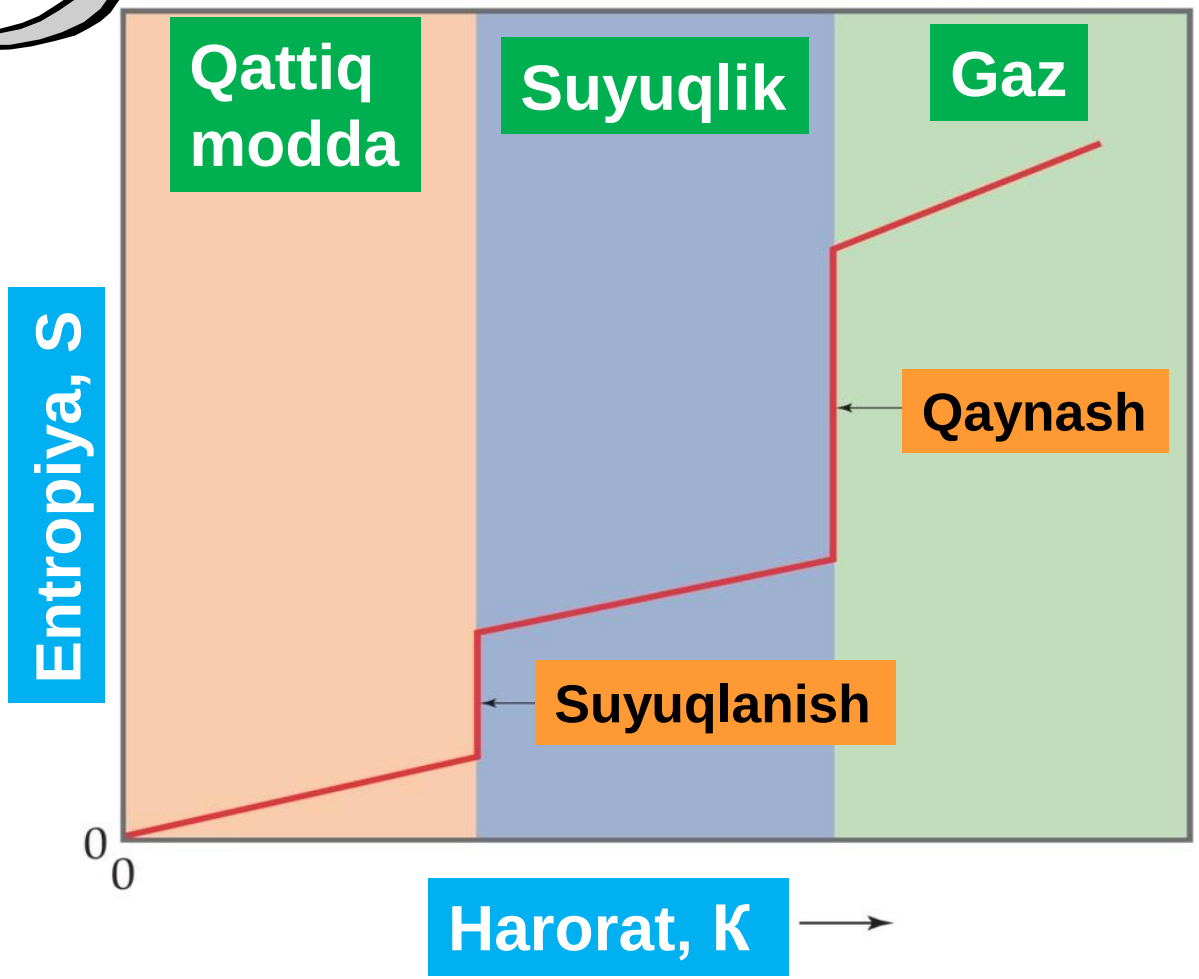


$S_{kristall} < S_{suyuq} < S_{gaz}$

<u>Entropiyasining o'sishi $\Delta S>0$,</u> tizimdagi tartibsizlikning kuchayishiga olib keladigan jarayonlar: suyuqlikning bug'lanishi, muzning erishi, moddalarning erituvchilarda erishi kabi o'z-o'zidan boruvchi jarayonlar bilan birga keladi.



Entropiya



<u>Entropiyasining pasayishi ΔS<0,</u> tizimdagi tartibning oshishiga olib keladigan jarayonlar, ya’ni, moddalarning kristallanish jarayonlari, polimerlanish reaksiyalari, polikondensatsiya kabilar bilan boradi.

Izobarik-izotermik potensial

Gibs energiyasi

$\Delta G = \Delta H - T\,\Delta S$ yoki $G = H - T\,S$

ΔG qiymati p=const va T=const (izobarik-izotermik sharoitda) 1 mol ideal gazning maksimal kengayish ishining o'lchovidir va shu bilan birga kimyoviy reaksiyalar o'z-o'zidan Gibbs energiyasi kamayib boruvchi qiymatlar tomon siljiydi.

$\Delta G < 0$ bo'lsa, reaksiya to'g'ri yo'nalishda boradi (o'z-o'zidan boradi)

$\Delta G > 0$ bo'lsa, reaksiya to'g'ri yo'nalishda bormaydi (o'z-o'zidan bormaydi)

$\Delta G = 0$ bo'lsa, tizim muvozanat holatida bo'ladi

Возможность самопроизвольной реакции в изолированной системе определяется сочетанием знаков энергетического (энтальпийного) и энтропийного факторов:

Знак ΔH	Знак ΔS	Возможность самопроизвольной реакции
+	–	Нет
–	+	Да
–	–	Зависит от соотношения ΔH и $T\Delta S$
+	+	Зависит от соотношения ΔH и $T\Delta S$

Haroratning ΔG qiymatga ta'siri:

1. ΔH>0, ΔS>0 bo'lganda, jarayon faqat yuqori haroratda o'z-o'zidan ketadi.

2. ΔH>0, ΔS<0 bo'lganda, jarayon har qanday haroratda o'z-o'zidan davom etadi (ketadi).

3. ΔH<0, ΔS>0 bo'lganda, jarayon har qanday haroratda o'z-o'zidan davom etadi (ketadi).

4. ΔH<0, ΔS<0 bo'lganda, jarayon faqat past haroratlarda o'z-o'zidan davom etadi (ketadi).

O’z-o’zidan boruvchi jarayonlar:

a) agar jarayon ekzotermik bo’lsa, $\Delta H<0$, $|\Delta H|\geq|T\Delta S|$.

$$\Delta G = -\Delta H - T\Delta S < 0$$

б) agar jarayon endotermik bo’lsa, $\Delta H>0$, $|\Delta H|<T\Delta S$, harorat yuqori bo’lishi lozim: $\Delta G = \Delta H - T\Delta S < 0$

Entalpiyaning ortishi harorat bilan boshqariladi, agar jarayon ishtirokchilari gazlar bo'lsa.

Agar $\Delta H > 0$, lekin $|\Delta H| > T\Delta S$ $\Delta G = \Delta H - T\Delta S > 0$

Izobarik-izotermik qiymat (ΔG) noldan katta bo’lsa, mazkur jarayon o’z-o’zidan bormaydi.

Standart sharoitda Gibbs energiyasi qiymati (ΔG^o f, 298): (stexiometrik koeffitsientlarni hisobga olgan holda) reaksiya mahsulotlarini hosil bo’lish standart Gibbs energiyalari yig'indisi bilan boshlang'ich moddalarni hosil bo’lish standart Gibbs energiyalari yig'indisi o'rtasidagi farqga teng:

$$\Delta G^{o}_{reaksiya} = \sum n_{mah.} \cdot \Delta G^{o}_{298\,mah.} - \sum n_{dast.\mathrm{mod.}} \cdot \Delta G^{o}_{298\,dastl.\mathrm{mod.}}$$

Oddiy sharoitda barqaror bo'lgan oddiy moddaning hosil bo'lish standart Gibbs energiyasi nolga teng.

$$CO\ (g) + H_2O\ (g) = CO_2\ (g) + H_2\ (g)$$

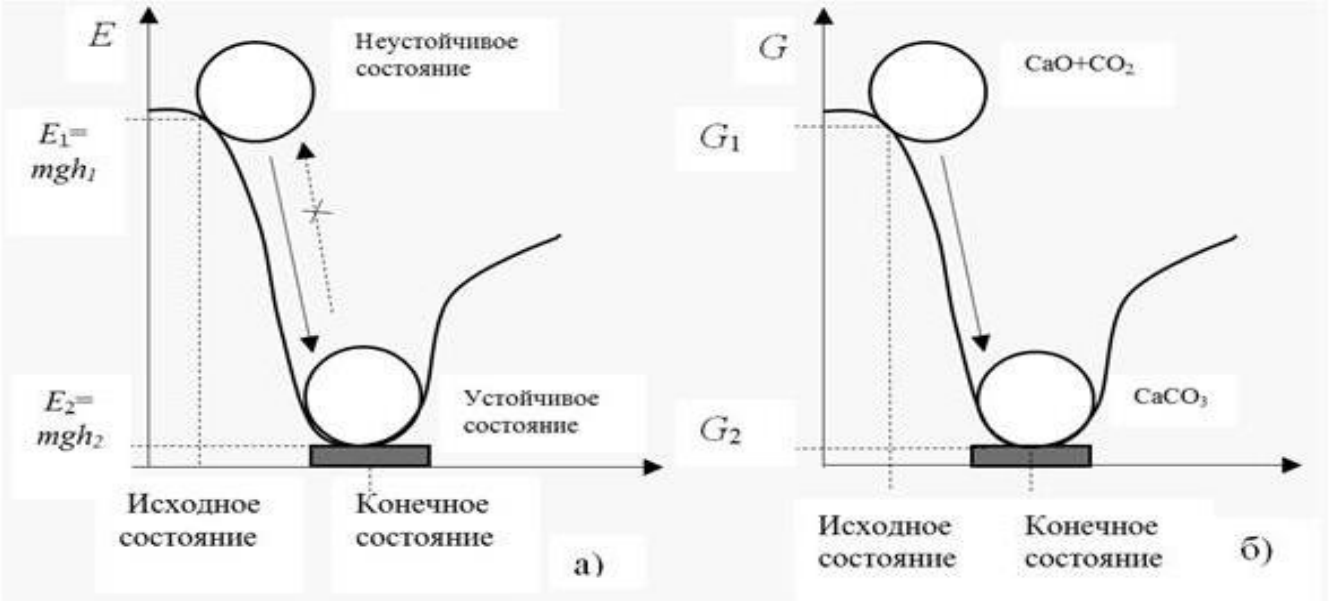
$$-137{,}176 \quad -228{,}66 \quad -394{,}47 \quad O$$

$$\Delta G^{o}r=|(-394{,}47+0)-(-137{,}16+(-228{,}66)|=-8{,}634\ kj/mol$$

$\Delta G^{o}r$ qiymati jarayonning o'z-o'zidan ketishini ko'rsatadi, ammo bu jarayonning tez yoki sekin borishini aniqlashga imkon bermaydi.

ΔH^{o} (CaO)=-177,4 kj/mol; ΔS^{o}(298)=0,16 kj/mol

$\Delta G^{o} = \Delta H - T\Delta S$=-177,4-(298(0,160))=- 129,72



Ba’zi moddalarning standart hosil bo’lish Gibbs energiyalari ($\Delta G^o_{f,\,298}$) qiymati

Modda	$\Delta G^o_{f,\,298}$, kj/mol	Modda	$\Delta G^o_{f,\,298}$, kj/mol
Al (q)	288,7	H_2O (s)	-237,24
Al^{3+}(s)	-490,54	H_2SO_4 (s)	-814,2
Al_2O_3 (q)	-1582,0	K^+ (s)	-281,3
$Al_2(SO_4)_3$ (s)	-3102,9	KCl (q)	-408,0
C (olmos)	2,83	$KClO_3$ (q)	-289,9
CH_4 (g)	-50,79	KNO_3 (q)	-393,1
CO (g)	-137,14	KOH (q)	-380,2
CO_2 (g)	-394,47	$MgSO_4$ (q)	-1158,7
$CaCl_2$ (g)	-750,2	$MgSO_{4*}7H_2O$ (q)	-2868
	-1128,8	H_2O (q)	455,5

Izolyatsiya qilingan tizimdagi har qanday o'z-o'zidan sodir bo'ladigan jarayon, agar jarayon qaytmas bo'lsa (muvozanat bo'lmasa) erkin energiyaning pasayishiga olib keladi; agar jarayon aksincha bo'lsa (muvozanat), u holda tizimning erkin energiyasi doimiy va minimal bo'ladi:

$$\Delta G \leq 0.$$

Agar sistemada (V=const; T=const), unda bunday termodinamik funksiya *izoxorik-izotermik (ΔF) yoki Gelmgols energiyasi* deb ataladi.

$$Q_V = \Delta U$$

$$\Delta F = \Delta U - T\Delta S$$

F=U-TS izoxorik-izotermik potensial.

ΔG, ΔF, ΔH va **ΔS holat funksiyalari bo'lib, ular tizimning bir holatdan ikkinchi holatga o'tishga bog'liq, lekin o'tish yo'llariga bog'liq emas.**

ΔG va ΔF reaksiyaga kirishuvchi moddalarning tabiati, massasi va haroratiga bog'liq.

ΔG tizim bosimiga bog'liq, ΔF o'z navbatida tizim hajmiga bog'liq.

Example Problem 20.1.1 Predict which substances have higher entropy.

Predict which substance in each pair has the higher entropy. Assume there is one mole of each substance at 25 °C and 1 bar.

a. $Hg(\ell)$ or $CO(g)$

b. $CH_3OH(\ell)$ or $CH_3CH_2OH(\ell)$

c. $KI(s)$ or $CaS(s)$

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Solution:

You are asked to choose the substance with the higher entropy at 25 °C.

You are given two substances and their physical states.

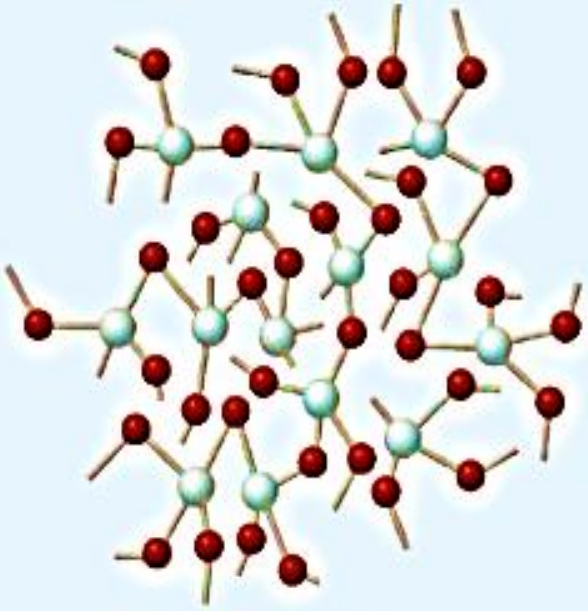
a. At 25 °C, carbon monoxide gas has a higher entropy than liquid mercury because the motion of the gas molecules is much more random than the motion of the mercury atoms in the liquid state.
b. Liquid ethanol, $CH_3CH_2OH(\ell)$, has a higher entropy than liquid methanol, $CH_3OH(\ell)$, because it is a larger, more complex molecule and therefore has a larger number of ways to distribute energy at a given temperature.
c. Potassium iodide, composed of K^+ and I^- ions, has a higher entropy than calcium sulfide, composed of Ca^{2+} and S^{2-} ions. In addition to the different ionic charges, KI contains ions with larger ionic radii. The entropy of ionic solids tends to increase as the attractive forces between the ions decrease because vibrational motion between the ions is easier.

Select the component in each of the following pairs of compounds that has the greater absolute entropy per mole at a pressure of 1 bar and 298 K.

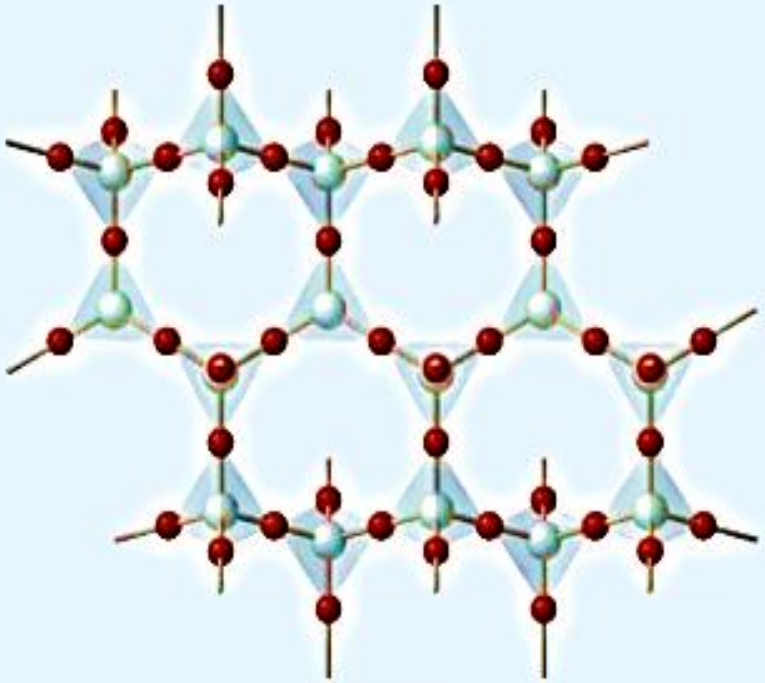
a. $HCl(g)$, $HCl(aq)$

b. $CH_3OH(\ell)$, $CH_3CH_2OH(\ell)$

c.



Obsidian
(amorphous SiO_2)



Quartz
(crystalline SiO_2)

Select the component in each of the following pairs of compounds that has the greater absolute entropy per mole at a pressure of 1 bar and 298 K.

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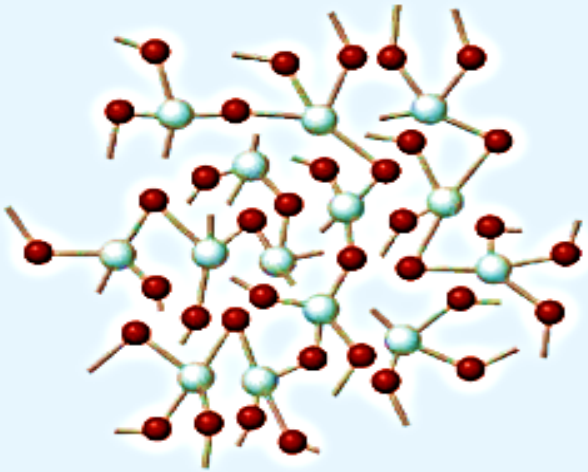
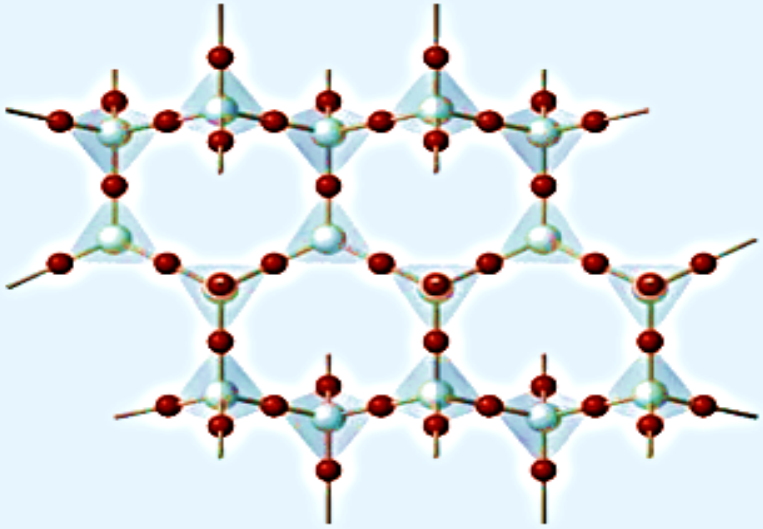


Obsidian
(amorphous SiO_2)



Quartz
(crystalline SiO_2)

Collect, Organize, and Analyze Particles in the vapor state have more freedom of motion and entropy than they do in the liquid state, and particles in the liquid state have more freedom of motion and entropy than they do in the solid state. Substances composed of more particles, contributing to more freedom of motion, have more absolute entropy than substances made of fewer particles with less freedom of motion.

E’tiboringiz uchun raxmat!