Advanced Soil Chemistry

Lecture 9

Prof. Dr.Hayfaa J. Al-Tameemi
Dep. of Soil Sci. and Water Resources
College of Agriculture/Univ. of Basra/IRAQ

الطاقة الحرة القياسية

Gibbs Free Energy

Gibbs Free Energy الطاقة الحرة القياسية

At constant temperature (T) and pressure(P) the change in Gibbs free energy is :-

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

لكي يحصل اي تفاعل يتحقق امرين عند التفاعلات التلقائية:ـ

١. اقل مستوى من الطاقة

٢. اعلى مستوى من العشوائية (الانتروبي S)

فالقوتين هي المسيرة لأي تفاعل كيميائي

At constant temperature ,negative values of ΔG indicate that the reaction should proceed spontaneously. Positive values indicate that the reaction cannot occur.

Or for spontaneous chemical and physical change, the Gibbs free energy change must be negative($\Delta G<0$)

For nonspontaneous reaction Gibbs free energy must be positive ($\Delta G>0$)

or the reaction A(reactant) $\longrightarrow$ B(product)

$$\Delta G = G_{products} - G_{reactants} \text{ (at constant T and)}$$

at equilibrium $\Delta G=0$ عند الاتزان

اذا كانت نواتج التفاعل الكيميائي في مستوى للانثالبية اوطئ من مستوى انثالبية المواد المتفاعلة (اي ΔH سالبة حيث ان التفاعل باعث للحرارة Exothermic) ومستوى الانتروبية عالية ΔS موجبة وكان التفاعل تلقائي وΔG سالبة.

اما اذا كانت النواتج في مستوى للانثالبية اعلى من مستواها للمواد المتفاعلة ΔH موجبة فان التفاعل ماص للحرارة Endothermic ومستوى الانتروبية عالي ΔS موجبة فان ΔG موجبة . اما اذا كان $\Delta H>T\Delta S$ في هذه الحالة لا يحصل تفاعل تلقائي .

Example 1

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

المطلوب: حساب التغير في الطاقة الحرة ΔG في درجة حرارة 298K (كلفن) تعادل (25° م)و 1000 ^{o} م .اذا علمت ان ΔH=178.3 كيلو جول.مول$^{-1}$ و ΔS=160.4 جول.مول$^{-1}$. درجة$^{-1}$.

الحل:-

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

$$= 178.3 K.joule.mole^{-1} - \frac{298 \ x \ 160.4}{1000}$$

$= + 108.0244$ K joule   التفاعل غير تلقائي   **nonspontaneous**

At 1000 ^{o}C equal to 1273.15 kelvin

$$\Delta G = 178.3 \ k \ , joule. \ mole \ ^{-1} \ - \frac{1273.15 \ x \ 160.4}{1000}$$

$$= - \ 25.91 \ k \ joule \ \textcolor{red}{spontaneous} \quad \text{التفاعل تلقائي}$$

هنا يتبين تأثير درجة الحرارة على التفاعل

ملاحظة Note

عندما تكون الظروف قياسية فأن ΔG يرمز لها ΔG^o

ΔG^o (تساوي الفرق بين مجموع الطاقات الحرة للتكوين القياسية للنواتج مطروحا من مجموع الطاقات الحرة للتكوين القياسية للمواد المتفاعلة) كل في الحالات القياسية

$$a \, A + b \, B \longrightarrow c \, C + d \, D$$

$$\Delta G^o = (\, cG^o_C + dG^o_D) - (aG^o_A + bG^o_B)$$

$$\Delta G_r^o = \sum \Delta G^o_{f \text{ products}} - \sum \Delta G^o_{f \text{ reactants}}$$

$$\Delta H_r^o = \sum \Delta H^o_{f \text{ products}} - \sum \Delta H^o_{f \text{ reactants}}$$

$$\Delta S_r^o = \sum \Delta S^o_{f \text{ products}} - \sum \Delta S^o_{f \text{ reactants}}$$

وقد تم الاتفاق عالميا بأن الطاقة الحرة للعناصر تساوي صفر (Lindsay,1979) .

Example 2

Calculate the standard free energy ΔGo for the reaction:-

$$H_2O_{(L)} \longrightarrow H_2O_{(g)}$$
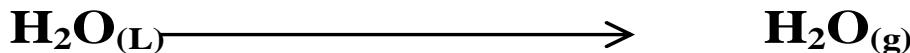
Data: | **Substance** | **ΔH^o(kJ.mole^{-1})** |
| --- | --- |
| **$H_2O_{(L)}$** | -273 |
| **$H_2O_{(g)}$** | -228 |

Solution :-

$$\Delta G_r{}^o = \sum \Delta G^o{}_{f\ products} - \sum \Delta G^o{}_{f\ reactants}$$

$$= \Delta G^o{}_{H2O(g)} - \Delta G^o{}_{H2O(L)}$$

$$= -228-(-237)$$

= 9 kj .mole^{-1}   **التفاعل غير تلقائي (ماص للحرارة)**

2.8 EQUILIBRIUM CONSTANTS FROM THERMODYNAMIC DATA

If chemical reactions proceed until the free energy (G) of a system reaches a minimum, then the system is at equilibrium. At equilibrium a system can do no more work on its environment without the input of additional energy. Since the absolute free energy of a substance is not measurable, reference states are selected for each substance and changes in free energy are then measured. The standard free energy change accompanying a chemical reaction (ΔG_r°) is the sum of the free energies of formation (ΔG_f°) of the products in their standard state minus the free energies of formation of the reactants in their standard states. That is,

$$\Delta G_r^\circ = \Sigma \Delta G_f^\circ \text{ products} - \Sigma \Delta G_f^\circ \text{ reactants} \qquad (2.29)$$

The standard free energy change of a reaction is related to the equilibrium constant of that reaction by the relationship:

$$\Delta G_r^\circ = -RT \ln K^\circ \qquad (2.30)$$

where K° is the activity equilibrium constant for the reaction, R is the universal gas constant, and T is the absolute temperature. At 25°C, Eq. 2.30 gives

$$\Delta G_r^\circ (\text{kcal}) = -0.001987 \text{ kcal deg}^{-1} \text{ mole}^{-1} \times 298.15 \text{ deg} \times 2.303 \log K^\circ$$

$$\Delta G_r^\circ = -1.364 \log K^\circ$$

$$\log K^\circ = -\frac{\Delta G_r^\circ}{1.364} \qquad (2.31)$$

This equation is extremely useful because it permits the calculation of equilibrium constants from thermodynamic data for reactions which are often difficult to measure by conventional methods. Except when noted otherwise, the equilibrium constants used throughout this text were calculated from Eq. 2.29 and 2.31 using the ΔG_f° values documented in the Appendix.

The standard free energy of a reaction (ΔG_r°) can be calculated from changes in the standard enthalpies of reaction (ΔH_r°) and changes in the standard entropies of reaction (ΔS_r°) by the relationship:

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ \qquad (2.32)$$

where

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants} \qquad (2.33)$$

and

$$\Delta S_r^\circ = \Sigma S^\circ \text{ products} - \Sigma S^\circ \text{ reactants} \qquad (2.34)$$

Once ΔG_r° is known, the standard free energy of any reactant or product can be determined from Eq. 2.29 providing ΔG_f° values of the other reactants and products are known.

EXAMPLE CALCULATION

Calculate the equilibrium constant for the reaction

$$AgCl(c) \rightleftharpoons Ag^+ + Cl^- \qquad (2.35)$$
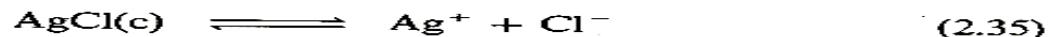
using the ΔH_f° and S° values given below from Sadiq and Lindsay (1979):

Species	ΔH_f° (kcal mole^{-1})	S° (cal deg^{-1} mole^{-1})
AgCl(c)	-30.370	23.00
Cl$^-$	-39.933	13.56
Ag$^+$	25.275	17.54
Ag(c)	0	10.17
e$^-$	0	15.603

$$\Delta H_r^\circ = 25.275 + (-39.933) - (-30.370) = 15.712 \text{ kcal mole}^{-1}$$
$$\Delta S_r^\circ = 17.54 + 13.56 - (23.00) = 8.10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$
$$= 15.712 - 298.15(0.00810)$$
$$= 13.297 \text{ kcal mole}^{-1}$$

and from Eq. 2.31

$$\log K^\circ = -\frac{13.297}{1.364} = \underline{-9.75}$$

From the following thermodynamic data   (Lindsay,1979,pp:32)

Species	ΔG^o_f(Kcal.)
e^-	0
H^+	0
OH^-	–37.594
Fe^{2+}	–21.80
Fe^{3+}	–4.02
$H_2O_{(l)}$	–56.687
$Fe(OH)_{3\ soil}$	–170.40
$Fe_3O_{4(magnetite)}$	–243.37

Calculate the following:-

a): The dissociation constant of water

b): log K^o for the reaction:-

    $Fe(OH)_{3\ soil}$ $\longleftrightarrow$ Fe^{3+} + 3 OH^-
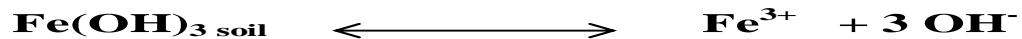
Solution:-

a)): H_2O $\longleftrightarrow$ H+ + OH-   (from Lindsay,1979   pp: 399)

$\Delta G_f = \sum \Delta G_{f\ products} - \sum \Delta G_{f\ reactants}$

    = [0 + (-37.594)] – [-56.687)]

    = 19.093 k cal.

$\Delta G = -2.303\ RT\ \log K_d$

$19.093 = -2.303 \times 1.987 \times 10^{-3}$ kcal. $.deg^{-1}.mole^{-1} \times 298.16\ ^oK \times \log K_d$

$19.093 = -1.3645\ \log K_d$

$\text{Log } K_d = \dfrac{-19.093}{1.3645}$

       $K = 10^{-13.9927}$

b)): $\quad Fe(OH)_{3\,Soil} \quad \longleftrightarrow \quad Fe^{3+} \quad + \quad 3OH^{-}$

$$\Delta G^{o}_{f} \quad = \quad -170.40 \qquad\qquad -4.02 \qquad 3(-37.594)$$

$$\Delta G^{o} = -2.303\ RT\ \log K^{o} = -RT\ \ln K^{o}$$

$$\Delta G_{r}^{o} = \sum \Delta G^{o}_{f\ products} - \sum \Delta G^{o}_{f\ reactants}$$

$$= [(-4.02)+ (-12.782)-(-170.40)]$$

$$= 53.598\ kcal.$$

$$\Delta G^{o} = -2.303\ RT\ \log K^{o}$$

$$53.598\ kcal.= -2.303 \times 1.98717 \times 10^{-3}\ kcal.deg^{-1}.mole^{-1}$$

$$\times 298.16\ ^{o}K \times \log K^{o}$$

$$\text{Log } K^{o} = -53.598/\ 1.3645$$

$$K^{o} = 10^{-39.28}$$

Thank u for your listening