Physical Chemistry for Energy Engineering
(18th: 2018/11/21)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (as of Nov. 5)

	29-Oct	No lecture
	31-Oct	
14	5-Nov	2. Phase equilibrium-1
15	7-Nov	2. Phase equilibrium-2
16	12-Nov	3. Chemical equilibrium-1
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-2
20	26-Nov	3. Chemical equilibrium-3
21	28-Nov	3. Chemical equilibrium-4
22	3-Dec	3. Chemical kinetics-1
23	5-Dec	3. Chemical kinetics-2
24	10-Dec	3. Chemical kinetics-3
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

Contents of today

<Last class>

2.3. Phase equilibrium-1: a typical case (1 component)

- 2.3.2. Freezing mechanism
- 2.3.x. Phase rule

<Today's class>

3.1. Chemical equilibrium for gases

3.1. Chemical equilibrium for gases

- $26: Introduction -

- ✓ Thermodynamics enables us to predict the equilibrium pressures or concentrations of reaction mixtures.
- ✓ In this chapter, we will derive a relation between the standard Gibbs energy change and the equilibrium constant for a chemical reaction.
- ✓ We will also learn how to predict the direction in which a chemical reaction will proceed if we start with arbitrary concentrations (thus, not equilibrium) of reactants and products.

- ✓ Although we need to utilize some equations specialized for gases, an important point is that chemical equilibrium (at const.-T const.-P condition) is governed by Gibbs energy as the same with phase equilibrium.
  - ✓ The equilibrium state is a state of the lowest Gibbs energy for chemical equilibrium, as the same with phase equilibrium (at const.-T const.-P)

3.1. Chemical equilibrium for gases
- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

The amount of species i is n_i [mol]. The Gibbs energy for this multi-component system is a function of $T, P, n_A, n_B, n_Y\ and\ n_Z$, then the total differential is:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B,n_Y,n_Z} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B,n_Y,n_Z} dP + \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z} dn_A$$
$$+ \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A,n_Y,n_Z} dn_B + \left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_A,n_B,n_Z} dn_Y + \left(\frac{\partial G}{\partial n_Z}\right)_{T,P,n_A,n_B,n_Y} dn_Z$$

Then, it can be re-written as:

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z}, etc$$

If the reaction takes place in const.-T const.-P condition,

$$\mathrm{d}G = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \qquad \text{(constant T and P)}$$

*This "const.-P" is about total pressure (not partial pressure).

3.1. Chemical equilibrium for gases

- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

We define a quantity ξ, called as the "extent of reaction". Here n_{i0} is the initial number of moles for species i, then :

$$n_A = n_{A0} - \nu_A \xi \qquad n_B = n_{B0} - \nu_B \xi \qquad \text{(reactants)}$$

$$n_Y = n_{Y0} + \nu_Y \xi \qquad n_Z = n_{Z0} + \nu_Z \xi \qquad \text{(products)}$$

In this case, ξ has units of moles. Then, the variations of n_i is:

$$dn_A = -\nu_A d\xi \qquad dn_B = -\nu_B d\xi \qquad \text{(reactants)}$$

$$dn_Y = \nu_Y d\xi \qquad dn_Z = \nu_Z d\xi \qquad \text{(products)}$$

*Note that the unit for $d\xi$ is [mol].

which means that as the reaction (left to right) proceeds, the reactants decrease and the products increase according to the stoichiometry.

Using these equations:

$$\begin{aligned} \mathrm{dG} &= \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \\ &= (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \qquad \text{(constant T and P)} \end{aligned}$$

3.1. Chemical equilibrium for gases

- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

$$\boxed{\mathrm{dG} = (-\nu_A\mu_A - \nu_B\mu_B + \nu_Y\mu_Y + \nu_Z\mu_Z)d\xi}$$

(constant T and P)

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B$$

Here, we define $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G$, which is the change in Gibbs energy when the extent of reaction changes by one mole, and its unit is $[\mathrm{J\ mol^{-1}}]$.

Assuming each species behaves as ideal gas, as the pressure dependence of chemical potential is written as $\mu_j(T,P) = \mu^\circ{}_j(T) + RT\ln\left(P_j/P^\circ\right)$, then:

$$\Delta_r G = \Delta_r G^\circ + RT\ln Q$$

$$Q = \frac{(P_Y/P^\circ)^{\nu_Y}\,(P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A}\,(P_B/P^\circ)^{\nu_B}}$$

P° is the pressure of standard state (1 bar) and P_A is the partial pressure of species A.

$$\Delta_r G^\circ = \nu_Y\mu^\circ{}_Y(T) + \nu_Z\mu^\circ{}_Z(T) - \nu_A\mu^\circ{}_A(T) - \nu_B\mu^\circ{}_B(T)$$

3.1. Chemical equilibrium for gases

- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

(ideal gas, constant T and P)

$$\Delta_r G^\circ = \nu_Y {\mu^\circ}_Y(T) + \nu_Z {\mu^\circ}_Z(T) - \nu_A {\mu^\circ}_A(T) - \nu_B {\mu^\circ}_B(T)$$

$$Q = \frac{(P_Y/P^\circ)^{\nu_Y}(P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A}(P_B/P^\circ)^{\nu_B}}$$

Here, the quantity $\Delta_r G^\circ$ is the change in standard Gibbs energy for the reaction between unmixed reactants to form unmixed products. All species in their standard states at T and P°. Note that $P^\circ = 1$ bar.

When the reaction system is equilibrium, the Gibbs energy must be the minimum with respect to any change from the equilibrium state, thus $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G = \Delta_r G^\circ + RT \ln Q_{eq} = 0$ at an equilibrium state. Thus:

$$\Delta_r G^\circ = -RT \ln \left(P_Y^{\nu_Y} P_Z^{\nu_Z} \big/ P_A^{\nu_A} P_B^{\nu_B} \right)_{eq} = -RT \ln K_P(T)$$

3.1. Chemical equilibrium for gases

- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

$$\Delta_r G° = -RT \ln K_P(T)$$

$$\Delta_r G° = \nu_Y \mu°_Y(T) + \nu_Z \mu°_Z(T) - \nu_A \mu°_A(T) - \nu_B \mu°_B(T)$$

$$K_P(T) = Q_{eq} = \left[\frac{(P_Y/P°)^{\nu_Y}\,(P_Z/P°)^{\nu_Z}}{(P_A/P°)^{\nu_A}\,(P_B/P°)^{\nu_B}}\right]_{eq} = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \times P°^{(\nu_A+\nu_B-\nu_B-\nu_B)}\right)_{eq}$$

$$P° = 1\ bar$$

*the subscript *eq* emphasizes that the partial pressures are in an equilibrium.

- ✓ $K_P(T)$ is called as *equilibrium constant*. Be sure that $K_P(T)$ has no unit.
- ✓ As seen in the definition, this constant is defined after the target equation is given.
  - ✓ For example, if the ν_A in the equation is changed (even keeping the same meaning of reaction, like $2\nu_A \mathrm{A(g)} + 2\nu_B \mathrm{B(g)} \rightleftharpoons 2\nu_Y \mathrm{Y(g)} + 2\nu_Z \mathrm{Z(g)}$), $K_P(T)$ value is changed.

3.1. Chemical equilibrium for gases

- $\mu_j(T,P) = \mu°_j(T) + RT\, ln\left(P_j/P°\right)$ for an ideal gas -

$$\boxed{\mu_j(T,P) = \mu°_j(T) + RT\ln\left(P_j/P°\right)}$$

For an ideal gas:

$$PV = nRT$$

$$U = nC_V T + constant. = nC_V T + nU_0$$ then d$U = nC_V dT$

For a path keeping some thermal equilibrium states (i.e. reversible process):

$$dU = TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{PdV}{T} = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

$$S(T,V) = \int nC_V\frac{dT}{T} + \int nR\frac{dV}{V} = nS_0 + nC_V\ln T + nR\ln V$$

$$G(T,V) = U + PV - TS = nC_V T + nU_0 + nRT - T\{nS_0 + nC_V\ln T + nR\ln V\}$$

3.1. Chemical equilibrium for gases

- $\mu_j(T,P) = \mu°_j(T) + RT\, ln\left(P_j/P°\right)$ for an ideal gas -

$$\boxed{\mu_j(T,P) = \mu°_j(T) + RT\ln\left(P_j/P°\right)}$$

$$G(T,V) = U + PV - TS = nC_V T + nU_0 + nRT - T\{nS_0 + nC_V \ln T + nR\ln V\}$$

$$G(T,P) - G(T,P_0) = -T\{nR\ln V\} + T\{nR\ln V_0\} = T_1\left\{nR\ln\frac{V_0}{V}\right\}$$

$$P_1V_1 = P_2V_2$$

$$G(T,P) - G(T,P_0) = T_1\left\{nR\ln\frac{V_0}{V}\right\} = T_1\left\{nR\ln\frac{P}{P_0}\right\}$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T}$$

$$\mu\,(T,P) = \mu\,(T,P°) + RT\ln\frac{P}{P°} = \mu°(T) + RT\ln\frac{P}{P°}$$

Here $P° = 1$ bar for the standard chemical potential.

3.1. Chemical equilibrium for gases

- $26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

(Example-1a) For reaction “3 H_2(g) + N_2(g) ⇌ 2 NH_3(g)”, the equilibrium pressures are given as P_{H2}, P_{N2}, and P_{NH3} .

$$K_{P,}(T) = \left(P_{NH_3}^2 \middle/ P_{H_2}^3 P_{N_2} \right)_{eq}$$

*Be sure that these pressures are pressures at equilibrium, as in the definition of equilibrium constant.

(Example-1b) For reaction “3/2 H_2(g) + ½ N_2(g) ⇌ NH_3(g)”, the equilibrium pressures are given as P_{H2}, P_{N2}, and P_{NH3} .

$$K_P(T) = \left(P_{NH_3} \middle/ P_{H_2}^{3/2} P_{N_2}^{1/2} \right)_{eq} \neq K_P(T)\ of\ example - 1a$$

Although the reactions themselves are identical, the equilibrium constants are not the same, because the equilibrium constant depends on the expression of chemical reaction equation.

3.1. Chemical equilibrium for gases

- $26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The equilibrium-constant expression for this reaction is:

$$K_{P,}(T) = \left({P_{PCl_3} P_{Cl_2}} \big/ {P_{PCl_5}} \right)_{eq}$$

Suppose we have 1 mol of PCl_5 (g) and no PCl_3 or Cl_2 at the beginning. When the reaction occurs to an extent ξ,

PCl_5: 1 mol → (1- ξ) mol

PCl_3: 0 mol → ξ mol, Cl_2: 0 mol → ξ mol

Total: 1 mol → (1+ ξ) mol

If ξ_{eq} is the extent of reaction at equilibrium, then the partial pressures are:

$$P_{PCl_3} = P_{Cl_2} = (\xi_{eq} P)/(1 + \xi_{eq}), \quad P_{PCl_5} = \big((1 - \xi_{eq})P\big)/(1 + \xi_{eq})$$

where P is the total pressure. Then, the equilibrium constant is:

$$K_{P,}(T) = \left({\xi_{eq}}^2 \big/ {1 - {\xi_{eq}}^2} \right) P$$

3.1. Chemical equilibrium for gases

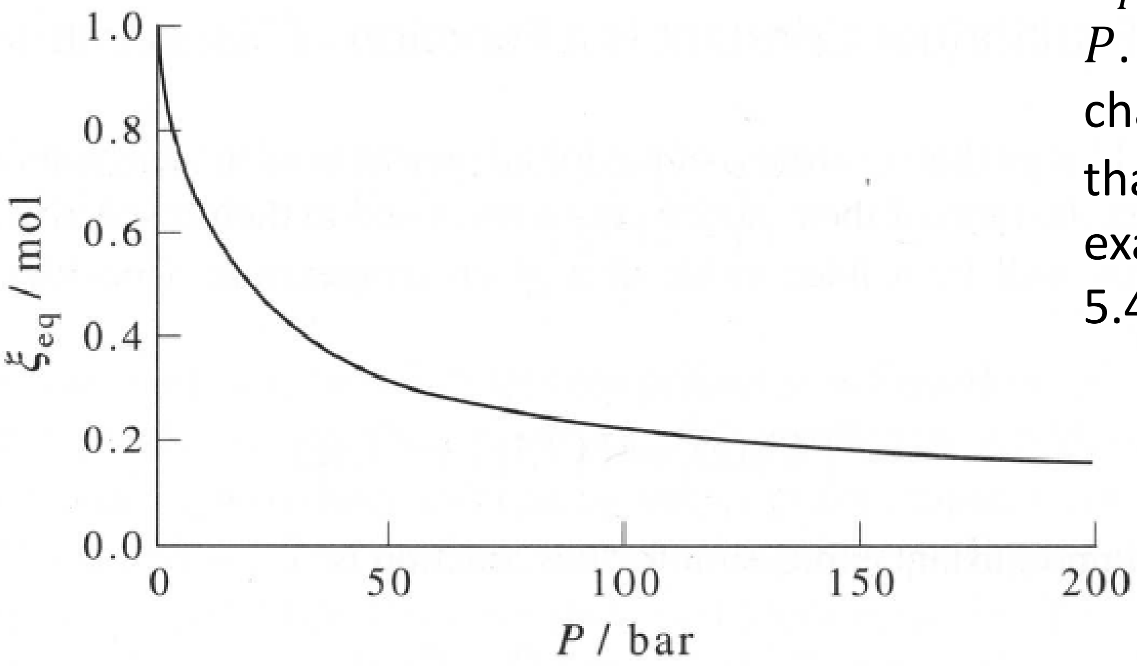
- $26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$K_P(T) = \left({\xi_{eq}}^2 \Big/ 1 - {\xi_{eq}}^2 \right) P$$

PCl$_5$: 1 mol → (1- ξ) mol
PCl$_3$, Cl$_2$: 0 mol → ξ mol,
Total: 1 mol → (1+ ξ) mol



*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

$K_P(T)$ only depends on T, but not P. So, if P (total pressure) is changed, ξ_{eq} must be changed so that $K_P(T)$ is kept constant. For example, $K_P(T)$ of this reaction is 5.4 (*no unit*) at 200ºC.

*If gases interact each other, $K_P(T)$ also depends on P. However, in practice, we can assume that gases behave like ideal gasses.

3.1. Chemical equilibrium for gases

- $26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

So far, we express the equilibrium constant regarding pressure. We can also express the equilibrium constant in terms of concentrations, etc, by using the ideal-gas relation "$P = cRT$", where $c = n/V$ is the concentration:

$$\Delta_r G° = -RT \ln K_P(T)$$

$$K_P(T) = Q_{eq} = \left[\frac{(P_Y/P°)^{\nu_Y} (P_Z/P°)^{\nu_Z}}{(P_A/P°)^{\nu_A} (P_B/P°)^{\nu_B}}\right]_{eq} = \left[\frac{C_Y^{\nu_Y} C_Z^{\nu_Z}}{C_A^{\nu_A} C_B^{\nu_B}}\right]_{eq} \left(\frac{RT}{P°}\right)^{\nu_Y+\nu_Z-\nu_A-\nu_B}$$

Here, we consider some standard concentration $c°$ (like $P°$), often taken to be "*1 mol L*$^{-1}$". Then:

$$K_P(T) = K_C(T) \left(\frac{c°RT}{P°}\right)^{\nu_Y+\nu_Z-\nu_A-\nu_B}$$

$$K_c(T) = \left[\frac{(c_Y/c°)^{\nu_Y} (c_Z/c°)^{\nu_Z}}{(c_A/c°)^{\nu_A} (c_B/c°)^{\nu_B}}\right]_{eq}$$

*As the same with K_P, K_c has also no unit.

3.1. Chemical equilibrium for gases

- $26-2: An equilibrium constant is a function of temperature only -

(Example-2) For reaction "$NH_3(g) \rightleftharpoons 3/2\ H_2(g) + 1/2\ N_2(g)$", $K_P(T) = 1.36 \times 10^{-3}$ at 298.15 K. Determine the corresponding $K_C(T)$.

$$K_P(T) = K_C(T)\left(\frac{c^\circ RT}{P^\circ}\right)^{3/2+1/2-1} = K_C(T)\left(\frac{c^\circ RT}{P^\circ}\right)^{1}$$

$$K_C(T) = K_P(T)\left(\frac{c^\circ RT}{P^\circ}\right)^{-1}$$

$$= 1.36 \times 10^{-3} \times \left[\frac{(1\ mol\ L^{-1}) \times (0.0831\ L\ bar\ mol^{-1}K^{-1}) \times (298.15\ K)}{1\ bar}\right]^{-1}$$

$$= 5.49 \times 10^{-5}$$

3.1. Chemical equilibrium for gases

- $26-3: Standard Gibbs energies of formation can be used to calculate equilibrium constants -

As already derived, K_P is related to the difference between the standard chemical potentials of the products and the reactants.

$$\Delta_r G^\circ = \nu_Y \mu^\circ{}_Y(T) + \nu_Z \mu^\circ{}_Z(T) - \nu_A \mu^\circ{}_A(T) - \nu_B \mu^\circ{}_B(T)$$

$$\Delta_r G^\circ = -RT \ln K_P(T)$$

Because a chemical potential is an energy (it is the molar Gibbs energy of a pure substance), we need to define a “zero” value.

As in the same manner with “standard molar enthalpy of formation”, we can define “the standard molar Gibbs energy of formation” according to

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

referring to standard molar entropies.

So, for “ν_AA(g) + ν_BB(g) → ν_YY(g) + ν_ZZ(g)”, for example, we have

$$\Delta_r G^\circ = \nu_Y \Delta_f G^\circ[Y] + \nu_Z \Delta_f G^\circ[Z] - \nu_A \Delta_f G^\circ[A] - \nu_B \Delta_f G^\circ[B]$$

where $\Delta_f G^\circ[Y]$ is the standard molar Gibbs energy of formation for substance Y.

3.1. Chemical equilibrium for gases

- how to calculate $\Delta_f G°$ -

We can find thermodynamic database, usually the one at 298.15 K (but not necessarily and not limited to):

- ✓ $\Delta_f H°$: Standard molar enthalpy (heat) of formation (kJ mol^{-1})
- ✓ $\Delta_f G°$: Standard molar Gibbs energy of formation (kJ mol^{-1})
- ✓ $S°$: Standard molar entropy at 298.15 K in (J mol^{-1} K^{-1})
- ✓ C_P: Molar heat capacity at constant pressure (J mol^{-1} K^{-1})

*As definition, the value is for 1 bar.

If the Gibbs energy is not available, you can calculate from enthalpy and entropy. For example, for H_2O(g) formation: "$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$"

$$\Delta_f G°(\mathrm{T\ K})[H_2O(\mathrm{g})]$$
$$= \left\{\Delta_f H°(\mathrm{T\ K})[H_2O(\mathrm{g})] - \Delta_f H°(\mathrm{T\ K})[H_2(\mathrm{g})] - \frac{1}{2}\Delta_f H°(\mathrm{T\ K})[O_2(\mathrm{g})]\right\}$$
$$- \mathrm{T}\left\{S°(\mathrm{T\ K})[H_2O(\mathrm{g})] - S°(\mathrm{T\ K})[H_2(\mathrm{g})] - \frac{1}{2}S°(\mathrm{T\ K})[O_2(\mathrm{g})]\right\}$$

By this way, as the same with the standard molar enthalpy of formation, pure elemental substances that appear as the equilibrium phase at the temperature have $\Delta_f G°(\mathrm{T\ K}) = 0$, and the standard molar Gibbs energies of other chemicals are aligned to them.

3.1. Chemical equilibrium for gases

- how to calculate $\Delta_f G°$ -

In addition, at constant pressure condition, temperature dependence of $\Delta_f G°(\mathrm{T\ K})$ can be evaluated using C_P as:

$$H°(T_2 K) = H°(T_1 K) + \int_{T_1}^{T_2} C_P dT$$

$$S°(T_2 K) = S°(T_1 K) + \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$G°(T_2 K) = H°(T_2 K) - T_2 S°(T_2 K)$$

where $H°$, $S°$ and $G°$ are molar enthalpy, molar entropy, and molar Gibbs energy. For evaluation of the standard Gibbs energy of formation, they can be replaced with $\Delta_f H°$, $S°$ and $\Delta_f G°$.

C_P is molar heat capacity at constant pressure. If T_2 is enough close to T_1, C_P can be regarded as a constant in most case.

3.1. Chemical equilibrium for gases

- $26-3: Standard Gibbs energies of formation can be used to calculate equilibrium constants -

(Example-3) Using the standard molar Gibbs energies of formation, calculate $\Delta_r G°$ and K_P at 298.15 K for

$$\mathrm{NH_3(g)} \rightleftharpoons 3/2\ \mathrm{H_2(g)} + 1/2\ \mathrm{N_2(g)}$$

$\Delta_f G°[NH_3(g)] = -16.637\ kJ\ mol^{-1}$, $\Delta_f G°[H_2(g)] = \Delta_f G°[N_2(g)] = 0\ kJ\ mol^{-1}$

$$\Delta_r G° = (3/2)\Delta_f G°[H_2(g)] + (1/2)\Delta_f G°[N_2(g)] - (1)\Delta_f G°[NH_3(g)]$$
$$= (3/2)(0) + (1/2)(0) - (1)(-16.637\ kJ\ mol^{-1}) = 16.637\ kJ\ mol^{-1}$$

$$\ln K_P(T) = -\frac{\Delta_r G°}{RT} = -\frac{16.637 \times 10^3\ J\ mol^{-1}}{(8.31\ J\ K^{-1}\ mol^{-1})(298.15\ K)} = -6.60$$

Hence, $K_P(T) = 1.36 \times 10^{-3}$ at 298.15 K.

3.1. Chemical equilibrium for gases

- $26-4: A plot of the Gibbs energy of a reaction mixture against the extent of reaction is a minimum at equilibrium -

Consider the thermal decomposition of N_2O_4 (g) at 298.15 K as an example to treat the Gibbs energy of a reaction mixture:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Suppose the initial state is "N_2O_4 (g) = 1 mol and NO_2 (g) = 0 mol" and the reaction brings the system to "N_2O_4 (g) = 1- ξ mol and NO_2 (g) = 2 ξ mol".

$$G(\xi) = (1-\xi)\bar{G}_{N_2O_4} + 2\xi\bar{G}_{NO_2}$$

$$= (1-\xi)\left\{G°_{N_2O_4} + RT\ln\left({}^{P_{N_2O_4}}/_{1\ bar}\right)\right\} + 2\xi\left\{G°_{NO_2} + RT\ln\left({}^{P_{NO_2}}/_{1\ bar}\right)\right\}$$

Here we assume the reaction occurs at a constant pressure ($P_{total} = 1\ bar$). Then, as the molar fraction is $x_{N_2O_4} = \frac{1-\xi}{1+\xi}$ for N_2O_4 and $x_{NO_2} = \frac{2\xi}{1+\xi}$ for NO_2:

$$P_{N_2O_4} = x_{N_2O_4}P_{total} = x_{N_2O_4}, \quad P_{NO_2} = x_{NO_2}P_{total} = x_{NO_2}$$

$$G(\xi) = (1-\xi)\left\{G°_{N_2O_4} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{G°_{NO_2} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

$$= (1-\xi)\left\{\Delta_f G°_{N_2O_4} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{\Delta_f G°_{NO_2} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

3.1. Chemical equilibrium for gases

- $26-4: A plot of the Gibbs energy of a reaction mixture against the extent of reaction is a minimum at equilibrium -

Consider the thermal decomposition of N_2O_4 (g) at 298.15 K and 1 bar as an example to treat the Gibbs energy of a reaction mixture:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

$$G(\xi) = (1-\xi)\left\{\Delta_f G^\circ{}_{N_2O_4} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{\Delta_f G^\circ{}_{NO_2} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

This equation gives the Gibbs energy of the reaction mixture, G, as a function of the extent of the reaction, ξ. Substituting the values for $\Delta_f G^\circ$:

$$G(\xi) = (1-\xi)\left\{97.8\ kJ\ mol^{-1} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{51.3\ kJ\ mol^{-1} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

3.1. Chemical equilibrium for gases

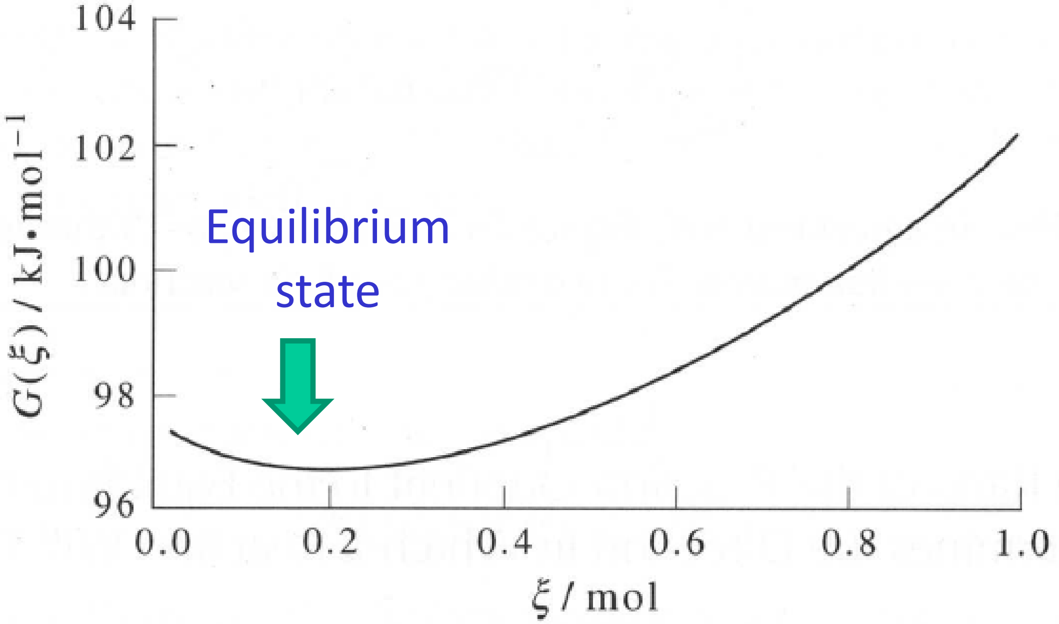
- $26-4: A plot of the Gibbs energy of a reaction mixture against the extent of reaction is a minimum at equilibrium -

Consider the thermal decomposition of N_2O_4 (g) at 298.15 K and 1 bar as an example to treat the Gibbs energy of a reaction mixture:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

$$G(\xi) = (1-\xi)\left\{97.8\ kJ\ mol^{-1} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{51.3\ kJ\ mol^{-1} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

Recall that $G(\xi)$ should take a minimum with respect to ξ at equilibrium state.



*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

FIGURE 26.2
A plot of the Gibbs energy of the reaction mixture versus the extent of reaction for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 298.15 K and one bar.

3.1. Chemical equilibrium for gases

- $26-4: A plot of the Gibbs energy of a reaction mixture against the extent of reaction is a minimum at equilibrium -

Consider the thermal decomposition of N_2O_4 (g) at 298.15 K and 1 bar as an example to treat the Gibbs energy of a reaction mixture:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

$$G(\xi) = (1-\xi)\left\{97.8\ kJ\ mol^{-1} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{51.3\ kJ\ mol^{-1} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

$G(\xi)$ is minimized at $\xi = 0.1892\ mol$, corresponding to the equilibrium state, thus $\xi = \xi_{eq} = 0.1892\ mol$.

Then, the equilibrium constant is:

$$K_P = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} = \frac{\left[2\xi_{eq}/(1+\xi_{eq})\right]^2}{(1-\xi_{eq})/(1+\xi_{eq})} = 0.148$$

We can also calculate it from $\Delta_r G°$:

$$\ln K_P = -\frac{\Delta_r G°}{RT} = -\frac{(2)\Delta_f G°[NO_2(g)] - (1)\Delta_f G°[N_2O_4(g)]}{(8.31\ J\ K^{-1}\ mol^{-1})(298.15\ K)} = -1.908$$

Hence, $K_P = 0.148$

3.1. Chemical equilibrium for gases

- $26-4: A plot of the Gibbs energy of a reaction mixture against the extent of reaction is a minimum at equilibrium -

Consider the thermal decomposition of N_2O_4 (g) at 298.15 K and 1 bar as an example to treat the Gibbs energy of a reaction mixture:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

$$G(\xi) = (1-\xi)\left\{97.8\ kJ\ mol^{-1} + RT\ln\frac{1-\xi}{1+\xi}\right\} + 2\xi\left\{51.3\ kJ\ mol^{-1} + RT\ln\frac{2\xi}{1+\xi}\right\}$$

We may also differentiate this equation with respect to ξ in order to find the minimum value where $(\partial G/\partial\xi) = 0$:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G^\circ + RT\ln\frac{{P_{NO_2}}^2}{P_{N_2O_4}}$$

Since $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$ at equilibrium,

$$\Delta_r G^\circ = -RT\ln\left(\frac{{P_{NO_2}}^2}{P_{N_2O_4}}\right)_{eq} = -RT\ln K_P$$

Solving $(\partial G/\partial\xi)_{T,P} = 0$ explicitly, $\xi_{eq} = 0.1892\ mol$ is obtained as well.

So, we confirmed that the equilibrium constant is defined to minimize the Gibbs energy for the reaction system.

3.1. Chemical equilibrium for gases
- $26-5: The ratio of the reaction quotient to the equilibrium constant determines the direction in which a reaction will proceed -

Consider a general reaction: ν_AA(g) + ν_BB(g) ⇌ ν_YY(g) + ν_ZZ(g)

$$\Delta_r G(T) = \Delta_r G°(T) + RT \ln\left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}}\right)$$

Realize that this equation is a general equation, so pressures are not necessarily the equilibrium pressures, but are arbitrary.

Generally, this equation gives the value of $\Delta_r G$ when
"A(g) of [ν_A mol at P_A bar] react with B(g) of [ν_B mol at P_B bar] to produce Y(g) of [ν_Y mol at P_Y bar] and Z(g) of [ν_Z mol at P_Z bar]".

1) If all the partial pressures are equal to 1 bar, $\Delta_r G(T) = \Delta_r G°(T)$. In other words, the Gibbs energy change will be equal to the standard Gibbs energy change.
    - ✓ But this may be unrealistic because this is not achieved in some cases if ν_i are not equal each other. For example, if "2 moles of A(g) and 1 mole of B(g)" coexist, $P_A \neq P_B$ and thus one of them must be not 1 bar.

      * $\Delta_r G° = \nu_Y \mu°_Y(T) + \nu_Z \mu°_Z(T) - \nu_A \mu°_A(T) - \nu_B \mu°_B(T)$
2) If the pressures are the equilibrium pressures, $\Delta_r G(T) = 0$ and then we obtain results that were derived in previous slides.

3.1. Chemical equilibrium for gases
- $26-5: The ratio of the reaction quotient to the equilibrium constant determines the direction in which a reaction will proceed -

Consider a general reaction: $\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$

$$\Delta_r G(T) = \Delta_r G^\circ(T) + RT \ln\left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}}\right)$$

By introducing a quantity called the "*reaction quotient*" $Q_P = \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}}$, and using an equation to correlate $\Delta_r G^\circ$ with K_P, $\Delta_r G^\circ = -RT \ln K_P$, then

$$\Delta_r G(T) = -RT \ln K_P + RT \ln Q_P = RT \ln(Q_P / K_P)$$

Note that this is not for the equilibrium; $\Delta_r G(T) = 0$ at equilibrium.

With this equation,

- ✓ At equilibrium, $\Delta_r G(T) = 0$ and thus $Q_P = K_P$.
- ✓ If $Q_P < K_P$, then Q_P must increase (because K_P is a constant) as the system proceeds toward equilibrium.
  - ➢ This is achieved by increasing the partial pressures of the products and decreasing those of the reactants. Hence, the reaction spontaneously proceeds from left to right.
- ✓ If $Q_P > K_P$, Q_P decrease as the system proceeds toward equilibrium.
  - ➢ In the same though, the reaction is spontaneous from right to left.

3.1. Chemical equilibrium for gases

- $26-5: The ratio of the reaction quotient to the equilibrium constant determines the direction in which a reaction will proceed -

(Example-4: #26-5) Consider " $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ ". The equilibrium constant $K_P = 10$ at 960 K. Calculate $\Delta_r G$ and check in which direction the reaction will proceed spontaneously for

$$2\,SO_2\,(1.0\times10^{-3}\ bar) + O_2\,(0.20\ bar) \rightleftharpoons 2\,SO_3(1.0\times10^{-4}\ bar)$$

$$Q_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(1.0\times10^{-4})^2}{(1.0\times10^{-3})^2(0.20)} = 5.0\times10^{-2}$$

Note that the value for Q_P is unitless because the definition of Q is, for example

in a general form, $Q = \dfrac{(P_Y/P^\circ)^{\nu_Y}\,(P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A}\,(P_B/P^\circ)^{\nu_B}}$ where $P^\circ = 1\ bar$.

$$\Delta_r G(T) = RT\ln(Q_P/K_P) = RT\ln(5.0\times10^{-2}/10) < 0$$

Hence, due to $\Delta_r G(T) < 0$ (or due to $Q_P < K_P$), the reaction proceed from left to right.

3.1. Chemical equilibrium for gases

- $26-6: The sign of $\Delta_r G$ and not that of $\Delta_r G°(T)$ determines the direction of reaction spontaneity -

It should be clearly understood that $\Delta_r G°$ is the value of $\Delta_r G$ when all the reactants and products are unmixed (which mean that they have not reacted) at partial pressures equal to 1 bar. Namely, $\Delta_r G°$ is the standard Gibbs energy changes. (recall that "standard" assumes 1 bar) Hence,

- ✓ If $\Delta_r G° < 0$, then $K_P > 1$, meaning that the reaction will proceed from reactants to products if all species are mixed at 1 bar (for each partial pressure; not total pressure).
- ✓ If $\Delta_r G° > 0$, then $K_P < 1$, thus reaction proceeds from products to reactants in the same condition.
- ✓ So, the sing of $\Delta_r G°$ just indicates the spontaneous reaction direction for the condition of $P_{partial} = 1$ bar (for all species of both reactants and products); not necessarily for all conditions.

3.1. Chemical equilibrium for gases

- $26-6: The sign of $\Delta_r G$ and not that of $\Delta_r G°(T)$ determines the direction of reaction spontaneity -

(Example-5) Consider " N_2O_4 (g) $\rightleftharpoons$ 2 NO_2 (g) ",
for which $\Delta_r G° = 4.729 \text{ kJ } mol^{-1}$ and $K_P = 0.148$ at 298.15 K.

First, make sure that this $\Delta_r G° > 0$ does NOT mean "no N_2O_4 dissociate at 298.15 K when we place some of N_2O_4 in a reaction vessel".
$\Delta_r G° > 0$ just means that "the chemical potential for N_2O_4 (g) of1 mol and1 bar is higher than that of NO_2 (g) of 2 mol and1 bar by $\Delta_r G°$ in comparison."

For correct interpretation, calculate $\Delta_r G$ to consider pressure dependence as:

$$\Delta_r G = \Delta_r G° + RT \ln Q_P = 4.729\ kJ\ mol^{-1} + (2.479\ kJ\ mol^{-1}) \ln\left(\frac{P_{NO_2}^2}{P_{N_2O_4}}\right)$$

If we just "place some of N_2O_4 in a reaction vessel", $\ln\left(P_{NO_2}^2/P_{N_2O_4}\right)$ has a large negative value, thus $\Delta_r G < 0$. Accordingly, some N_2O_4 dissociate.

The equilibrium state is achieved by the condition $\Delta_r G = 0$ (note $\Delta_r G°$ is a constant while $\Delta_r G$ changes depending on P_{NO_2} and $P_{N_2O_4}$), at which point $Q_P = K_P$. Until this point is achieved, P_{NO_2} increases and $P_{N_2O_4}$ decreases.