CBEg 6162- Advanced Chemical Engineering Thermodynamics

Chemical Reaction Equilibrium

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Reaction equilibrium

- An important application of ***statistical thermodynamics*** is to predict ***the equilibrium constant for gas phase reactions***. In this section ***the prediction of chemical equilibrium constant in an ideal gas mixture*** is discussed. Generally, *the equilibrium constant predicted by the application of statistical thermodynamics are considered to be more accurate than the experimental values* in view of the inaccuracies associated with the measurement.

Equilibrium Constant-Classical Thermodynamics Approach

- The criteria for equilibrium are expressed in terms of the fundamental relation as
    - ***S is maximum or dS=0 (at constant U,V)***
    - ***U is minimum or dU=0 (at constant S,V)***
    - ***A is minimum or dA=0 (at constant T,V)***
    - ***H is minimum or dH=0 (at constant S,P)***
    - ***G is minimum or dG=0 (at constant T,P)***
- Based on the condition of the chemical reaction, the appropriate criterion can be employed to ***estimate the equilibrium constant***. Usually; ***the chemical reactions are carried out at constant temperature and pressure***. Therefore ***the fundamental relation in the Gibbs free energy representation is used to estimate the equilibrium constant.***

Chemical reactions

- The equilibrium constant can be estimated from the ***criterion dG=0 at constant T and P as shown below.***
- Consider the following chemical reaction

$$aA + bB \longrightarrow cC + dD$$

Where A, B, C, D represent the chemical species and a, b, c, d are the stochiometric coefficients. The convenient way of representing the above chemical reaction is

$$v_1 A_1 + v_2 A_2 + v_3 A_3 + v_4 A_4 = 0 \text{ or } \sum v_i A_i = 0$$

- Where A_1…., A_4 represent the chemical species and v_1… v_4 are the stochiometric coefficients. The stochiometric coefficient associated with a reactant is assigned a negative sign since the reactant is consumed while the reaction proceeds, the coefficients associated with the product is assigned a positive sign as a product is formed in the reaction.

Chemical species

- The mole numbers of the chemical species are not independent, but they are related to the stochiometric coefficients as given below

$$dN_i = v_i d\xi$$

- Where ξ is the extent of reaction which characterizes the degree of conversion or extent to which the reaction proceeds
- For the chemical reaction system, ***the criterion of equilibrium at constant temperature and pressure reduces to*** $\sum v_i \mu_i = 0$. Where μ_i is the chemical potential of species i.
- For an ideal gas (single component system), the change in Gibbs free energy is given by $dG = -SdT + VdP$ .Hence, at constant temperature, the change in the ***Gibbs free energy can be expressed as*** $dG = VdP = RT\frac{dP}{P} = RTd\ln P$ ***(at constant T)***

- This equation can be modified for the real gases the change ***in the Gibbs free energy can be expressed as*** $dG = RdT(\ln f)$
- Where ***f*** is called ***the fugacity which has the dimension of pressure.*** The term fugacity was introduced by ***Gilbert Newton Lewis to express the behavior of real gases***. At sufficiently low pressures (P→ 0), all real gases behave an ideal gases. Hence ***the fugacity of the gas should be equal to its pressure at very low pressure***. That is $\frac{f}{P} \rightarrow 1 \text{ as } p \rightarrow 0$
- When μ_I is expressed in terms of G_i^o , the standard state Gibbs free energy of species *i and* a_i, the activity of species i, the criterion of equilibrium yields the following relation.

Equilibrium relation

$$\Delta G^o = -RT \ln K_a$$

- Where $\Delta G^o = \sum v_i \mu_i^o =$ Standard Gibbs free energy change for the reaction and K_a is the equilibrium constant and it is a function of temperature only and given by $K_a = \exp\left(\frac{-\Delta G^o}{RT}\right)$ where $K_a = \prod_i a_i^{v_i}$
- In an ideal gas reaction mixture the relation of this equation can be written as $K_a = \prod_i a_i^{v_i} = \prod_i p_i^{v_i} = K_p$

Where K_p is the equilibrium constant expressed in partial pressures of components. The equilibrium composition of a mixture is given by

$$K_a = K_p = K_y P^{\Sigma v_i} \text{ where } K_y = \prod_i y_i^{v_i}$$

- Most of the chemical reactions are carried out at temperatures other than 298.15K. The effect of temperature on the equilibrium constant can be obtained as

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G^o}{T}\right)\right]_P = \frac{1}{T}\left[\frac{\partial(\Delta G^o)}{\partial T}\right] - \frac{\Delta G^o}{T^2} \text{ since } \Delta G^o = \Delta H^o + T\left[\frac{\partial(\Delta G^o)}{\partial T}\right]_P \text{ we get}$$

$$\left[\frac{\partial(\Delta G^o)}{\partial T}\right]_P = -\frac{\Delta H^o}{T^2} \text{ since } \frac{\Delta G^o}{T} = -R\ln K \text{ we get}$$

$$\left[\frac{\partial \ln K}{\partial T}\right]_P = \frac{\Delta H^o}{RT^2}$$

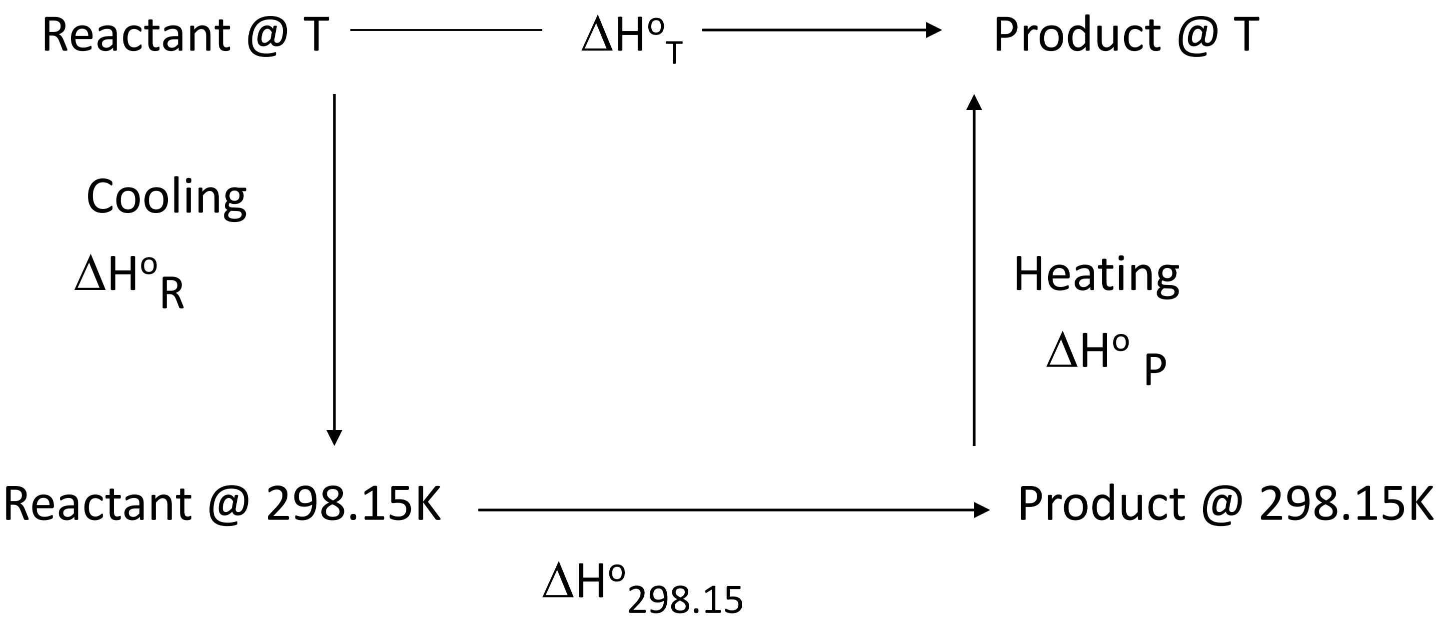
- This is known as Vant Hoff’s equation.

- From this equation we can observed that for an endothermic reaction ($\Delta H^{o} < 0$), i.e. the product possess more energy than reactants), the equilibrium constant increases with increasing temperature. On the other hand, for an exothermic re ($\Delta H^{o} > 0$) i.e. the products possess less energy than reactants), the equilibrium constant deceases as the temperature is increased.
- If ΔH^{o} is constant over a small rang of temperature this equation can be integrate to obtain equation which lacks to include the effect of temperature in determining ΔH^{o}.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^{o}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Including effect of temperature in determining ΔHo

Entropy depends on initial and final values.



Reactant @ T — ΔH^o_T → Product @ T

Cooling

ΔH^o_R

Heating

ΔH^o_P

Reactant @ 298.15K → Product @ 298.15K

$\Delta H^o_{298.15}$

$$\Delta H^o_T = \Delta H^o_{298.15} + \Delta H^o_R + \Delta H^o_P$$

Cont’d…

The change in enthalpy of the reactants and products can be expressed as;

$$\Delta H_R^o = \int_T^{298.15} \sum \left(V_i C_{P_i}^o dT \right)_R$$

$$\Delta H_P^o = \int_{298.15}^{T} \sum \left(v_i C_{P_i}^o dT \right)_P$$

into enthalpy relation.

$$\Delta H_T^O = \Delta H_{298}^O + \int_{298}^{T} \sum \left(v_i C_{P_i}^o dT \right) *$$

But heat capacities are given by;

$C_p^o = a + bT + CT^2$ (constant P)**

Substituting eqn*. into eqn. **, integrating and collecting terms,

Cont’d…

$$\Delta H_T^o = \Delta H_o + \Delta a T + \frac{\Delta b T^2}{2} + \frac{\Delta c T^3}{3}$$

Where, $\Delta a = \Sigma a_i v_i$, or $(\Sigma av)_{pdct} - (\Sigma av)_{react}$

$\Delta b = \Sigma b_i v_i$

$\Delta c = \Sigma c_i v_i$

$\Delta H_o = \Delta H^o_{298} - 298.15\, \Delta a - (298.15)^2\, \Delta b/2 - (298.15)^3\, \Delta c/3$

= Constant

substituting the above eqn. into Vant Hoff’s eqn.

Finally, $\ln k = \frac{1}{R}\left\{\frac{-\Delta H_o}{T} + \Delta a \ln T + \frac{\Delta b}{2} T + \frac{\Delta c}{6} T^2\right\} + I$

Where, I Integration constant,

Example 1

Estimate the equilibrium constant at 298.15K for the production of Methanol according to the reaction

$$CO + 2H2 \longrightarrow CH3OH$$

Example 2

The equilibrium constant for the reaction

$$\mathbf{CO + H_2O \longrightarrow CO_2 + H_2}$$

at a specified T and P is 2. If a mixture of CO and H_2O in the mole ratio 1:1 is fed to a reactor which is maintained at T and 0.1 Mpa pressure, determine the degree of conversion of H_2O into H_2 and the composition of the equilibrium mixture.

Example 3

The equilibrium constant for the reaction

$$\mathbf{CO + 2H2 \longrightarrow CH3OH}$$

Is 2.204X104 at 298.15 K. Given that the standard enthalpy change for this reaction is -90.135kJ. Estimate the equilibrium constant at 400K, assuming that $\Delta H0$ is constant in the temperature range 298.15 K to 400K.

Example 4

Determine the standard enthalpy change at 298.15K for the following reactions

a) $\mathrm{CO + 2H2} \longrightarrow \mathrm{CH3OH}$

b) $\mathrm{2CO + 4H2} \longrightarrow \mathrm{2CH3OH}$

Example 5

Estimate the equilibrium constant at 400 K for the reaction

$$\mathrm{CO + 2H2 \longrightarrow CH3OH}$$

Given that K298.15 = 2.204 X104 and ΔH0298 = -90.135kJ

EQUILIBRIUM CONSTANT - STATISTICAL THERMODINAMICS APPROACH

- . From the rxn $aA+bB \rightarrow cC+dD$ By applying classical thermodynamics relation and statistical mechanical approach, we obtain a relation Kc for ideal gas mixture.
- In case of classical the Chemical potential is given by

$$\mu = -KT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = -KT\ln\left(\frac{q}{N}\right)$$

- consider binary s/m:N1,N2 occupying a volume V at T. Then canonical ensemble PF

$$Q = \frac{q_1^{\ N_1} q_2^{\ N_2}}{N_1!N_2!}$$

- We can obtain μ_1 in this mixture as

$$\mu_1 = -KT\ln\left(\frac{q_1}{N_1}\right)$$

Cont'd…..

$$\sum_i \mu_i \nu_i = 0$$

- Substituting $\mu_1 = -KT \ln\left(\frac{q_1}{N_1}\right)$ in the above equation

$$\sum \nu_i \mu_i = -KT \sum \nu_i \ln\left(\frac{q_i}{N_i}\right) = 0$$

$$\sum \nu_i \ln q_i - \sum \nu_i \ln N_i = \ln \prod_i q_i^{\nu_i} - \ln \prod_i N_i^{\nu_i} = 0$$

$$\prod_i q_i^{\nu_i} = \prod_i N_i^{\nu_i}$$

- Since, $q = q_t q_r q_v q_e$
- translational PF $q_t = Vf(T)$
- The rotational, vibrational and electronic PF are function of Temp. only.

$$q = q_t q_r q_v q_e = Vf(T) \qquad \frac{q}{v} = f(T)$$

Cont'd…..

- K_c is function of temp. only and related to K_p

$$K_c = \prod_i \left(\frac{N_i}{V}\right)^{\nu_i} = \prod_i \left(\frac{p_i}{kT}\right)^{\nu_i} = (kT)^{\Sigma\nu_i} \prod_i p_i^{\nu_i} = (kT)^{-\Sigma\nu_i} K_p$$

$$K_p = (kT)^{\Sigma\nu_i} K_c = \prod_i \left(\frac{q_i kT}{V}\right)^{\nu_i}$$

- In the case of statistical & mechanical approach the probability fraction of molecule in the quantum state ε_J

$$P_J = \frac{N_J}{N} = \frac{\exp\left(\frac{-\varepsilon_J}{kT}\right)}{\sum \exp\left(\frac{-\varepsilon_J}{kT}\right)} = \frac{\exp\left(\frac{-\varepsilon_J}{kT}\right)}{q}$$

Where N_J is the number of molecules in quantum state ε_J

and N is the total number of molecules.

Cont'd…..

- Suppose we consider quantum states i, j, k as one group and interested in finding the probability

$$p(group) = p_i + p_j + p_k = \frac{N_i + N_j + N_K}{N} = \frac{\exp\left(\frac{-\varepsilon_i}{kT}\right)}{q} + \frac{\exp\left(\frac{-\varepsilon_J}{kT}\right)}{q} + \frac{\exp\left(\frac{-\varepsilon_k}{kT}\right)}{q} = \frac{q(group)}{P}$$

$$where q(group) = \exp\left(\frac{-\varepsilon_i}{kT}\right) + \exp\left(\frac{-\varepsilon_J}{kT}\right) + \exp\left(\frac{-\varepsilon_J}{kT}\right)$$

- Suppose the quantum states groups in to a, b, c, … such that no quantum state is present in more than one group, then the relative probability of observing a molecule in groups a and b is

$$\frac{p(groupa)}{p(groupb)} = \frac{N_a}{N_b} = \frac{q(groupa)}{q(groupb)}$$

Cont’d…..

- Consider 1,2 dichloroethylene,the cis- to trans-conversion in the presence of catalyst.

$$K_c = \frac{N_{trans}}{N_{cis}} = \frac{q_{trans}}{q_{cis}}$$

- For a chemical reaction involving more than two species

$$CO + H_2O \rightarrow CO_2 + H_2$$

- The reaction system contains the atom C,O, H to form CO,H_2O,CO_2 and H_2.

$$q(CO) = \sum_{co-state} \exp\left(\frac{-\varepsilon_i}{kT}\right)$$

Cont'd…..

- The same for others. Therefore the total partition function

$$q(total) = \sum_{allstates} \exp\left(\frac{-\varepsilon_i}{kT}\right)$$

- The fraction of molecule at equilibrium given by

$$\frac{N_{CO}}{N_{total}} = \frac{q(CO)}{q(total)}$$

- Then K_C becomes

$$K_c = \frac{(N_{CO_2})(N_{H_2})}{(N_{CO})(N_{H_2O})} = \frac{q(CO_2)q(H_2)}{q(CO)q(H_2O)}$$

or

$$K_c = \frac{\left(\frac{N}{V}\right)_{CO_2}\left(\frac{N}{V}\right)_{H_2}}{\left(\frac{N}{V}\right)_{CO}\left(\frac{N}{V}\right)_{H_2O}} = \frac{\frac{q}{v}_{(CO_2)}\frac{q}{v}_{H_2}}{\frac{q}{v}_{(CO)}\frac{q}{v}_{(H_2O)}}$$

Then for the general reaction aA + bB → cC + dD KC is given by

$$K_c = \prod_i \left(\frac{N_i}{V}\right)^{v_i} = \prod_i \left(\frac{q_i}{V}\right)^{v_i}$$

ISOMERIZATION REACTION

- Suppose an isomerization rxn is given by

$$\mathrm{A} \rightarrow \mathrm{B}$$

- Therefore K_C becomes

$$K_c = \frac{N_B}{N_A} = \frac{q_B}{q_A} = \frac{\sum \exp\left(\frac{-\varepsilon_B}{kT}\right)}{\sum \exp\left(\frac{-\varepsilon_A}{kT}\right)}$$

- This equation shows that the energy and the number of quantum states of A&B determine the equilibrium composition N_A & N_B.

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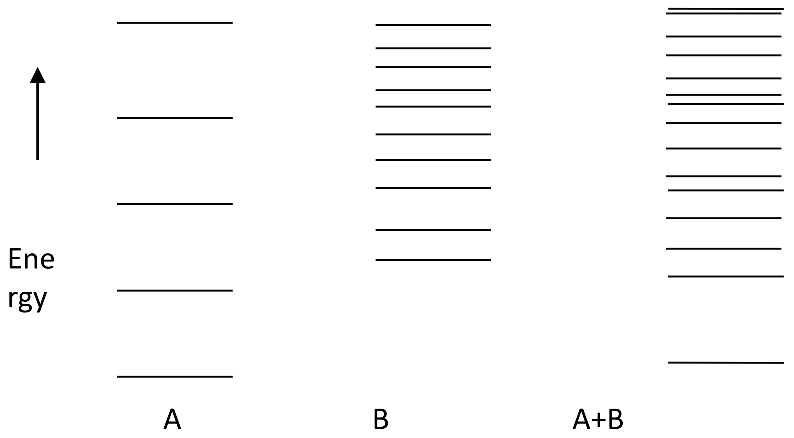
- Suppose The energy states of A and B are shown



- ➢ Energy state of A are lower than B ,since A and B have the same mass, their translational energy states would be identical
- ➢ the ground electronic energy of A is lower than that of B, A can have low lying energy state. This shows the dissociation of energy A is more stable than B.

Isotopic exchange reaction equilibrium

- For isotopic exchange reaction $A_2 + B_2 \longrightarrow 2AB$ Where A_2, B_2 and $2AB$ are isotopes. The equilibrium constant K_c for this reaction is given by:

$$Kc = \frac{(N_{AB})^2}{N_{A_2} N_{B_2}} = \frac{q^2{}_{AB}}{q_{A_2} q_{B_2}} = K_t K_r K_v K_e$$

- Where K_t, K_r, K_v ,K_e, are the transitional, rotational, vibrational and electronic factors of K_c respectively
- The calculations of K_c for this reaction can be simplified by making use of the Born Oppenheimer approximation.

Cont'd….

- The Born –Oppenheimer approximation Leads to several isotopic exchange reaction

u_e is the same function for $A_{2,} B_{2,} AB$

- Therefore, the depth of the potential well D_e, the inter molecular separation r_e and the force constant f are the same for all three species

- since, $D_e = - \varepsilon_e$

$$q_e = g_{el} \exp\left(\frac{\varepsilon_e}{k\mathrm{T}}\right) = g_{el} \exp\left(\frac{D_e}{kT}\right)$$

$$\mathrm{K}_e = \frac{\left(q_e\right)_{AB}{}^2}{\left(q_e\right)_{B_2}\left(q_e\right)_{A_2}} = 1$$

Cont’d….

- Since $A_{2,} B_{2,} AB$ have the same $(q_e)_{AB} = (q_e)_{A_2} = (q_e)_{|B_2}$ as (D_e)
- The translational pf

$$q_t = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} (v)$$

- Then K_t reduces to

$$k_t = \left(\frac{(m_{\mathrm{A}} + m_{\mathrm{B}})^3}{(2m_{\mathrm{A}})^{3/2} (2m_{\mathrm{B}})^{3/2}} \right)$$

- The rotational pf

$$q_r = \left(\frac{\mathrm{T}}{(\sigma)(\theta_r)} \right) = \left(\frac{(8\pi^2)(Ik)(T(\ \ ))}{(\sigma)(h^2)} \right)$$

- σ = 2 for A_2 and B_2 , σ =1 for AB

$$k_r = \left(\frac{4{I_{\mathrm{AB}}}^2}{(I_{\mathrm{A}_2})(I_{\mathrm{B}_2})} \right) = \left(\frac{16 m_A m_B}{(m_{\mathrm{A}} + m_{\mathrm{B}})^2} \right)$$

Cont'd….

- The vibrational function

$$q_\nu = \left(\frac{\exp\left(-\theta_\nu / 2T \right)}{\left(1 - \exp\left(-\theta_\nu / T \right) \right)} \right)$$

- By rearranging and substituting

$$k_\nu = \left[\frac{-\left(\exp\left(-\theta_\nu / 2T \right) \right)_{\mathrm{AB}}^{2}}{\left[\exp\left(-\theta_\nu / 2T \right) \right]_{\mathrm{A}_2} \left[\exp\left(-\theta_\nu / 2T \right) \right]_{\mathrm{B}_2}} \right]$$

- For diatomic molecule θ_v is large

- At ordinary temperature $\exp\left(\frac{-\theta_\nu}{T} \right)$ is very small

Example 6

Calculate the equilibrium constant K for the following reactions at 300 K for the production of Methanol according to the reaction

$$H_2 + D_2 \longrightarrow 2HD$$

Given $\theta_v (H_2) = 6210$ *K.*