

Thermodynamics Review

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3.2.3 Reversible Reactions

- Before we proceed, let's review some thermodynamics since we will be dealing a lot with reversible, equilibrium reactions.

- For the rxn $2A \leftrightarrow B$,

$$K_{C1} = \frac{C_{Be}}{C_{Ae}^2} \quad \& \quad \Delta H_{rxn1}^{\circ} = \Delta H_{f,B}^{\circ} - 2 \Delta H_{f,A}^{\circ} \quad [J] \text{ or } [J/2 \text{ mol } A]$$

- While if the same rxn is written as $A \leftrightarrow \frac{1}{2} B$, then

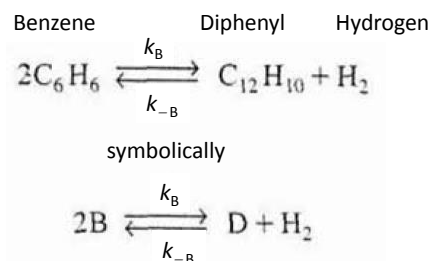
$$K_{C2} = \frac{C_{Be}^{0.5}}{C_{Ae}} \quad \& \quad \Delta H_{rxn2}^{\circ} = 0.5 \Delta H_{f,B}^{\circ} - \Delta H_{f,A}^{\circ} \quad [J] \text{ or } [J/\text{mol } A]$$

- Where $K_{C1} = (K_{C2})^2$ & $\Delta H_{rxn1}^{\circ} = 2 \times \Delta H_{rxn2}^{\circ}$

- $\therefore$ For thermodynamics calculations, rxns are considered as written

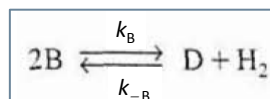
3.2.3 Reversible Reactions

- Consider the following reaction:



- In this discussion, we shall consider this gas-phase rxn to be elementary & reversible.

- For the benzene rxn, $K_C = \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{C_{\text{Be}}^2}$



where K_C represents the **Concentration Equilibrium Constant**.

- What is **Equilibrium Constant** to begin with?

- Remember the criterion of chemical-reaction equilibrium?

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

- From this criterion, the following equation is derived:

$$\prod_i \left(\hat{f}_i / f_i^\circ \right)^{\nu_i} = \exp \left(\frac{-\Delta G^\circ(T)}{RT} \right)$$

where $\hat{f}_i$ is the fugacity of species i in solution/mixture

and f_i° is the standard state fugacity of species i .

What are the conditions of standard state?

Standard-State at given T : 1 bar, pure species, specified physical state.

Could you please remind us what fugacity is?

Ref: Wikipedia.org,
Smith & Van Ness

In chemical thermodynamics, the **fugacity** (f_i) of a real gas is the corrected pressure (**effective pressure**) which replaces the actual (mechanical) pressure in accurate *chemical equilibrium calculations*.

For example, N₂ at 0°C and a pressure of 100 atm has a fugacity of 97 atm.

The fugacity coefficient (for pure gases) is defined as: $\phi_i \equiv f_i / P$

So what is ϕ_{N_2} at 0°C & 100 atm? The ϕ_{N_2} is just 0.97 with no units.

Steam at 300°C & 4,000 kPa has a fugacity of 3,611 kPa and, therefore, a fugacity coefficient of 0.903.

While steam at 300°C & 1 kPa has a fugacity of 1 kPa and, therefore, a fugacity coefficient of 1.0 (ideal gas).

If effective pressure is called fugacity, then what effective concentration is called?

Ref: Wikipedia.org,
Smith & Van Ness

The effective concentration is represented by a quantity called “activity” which is given the symbol (a).

In chemical thermodynamics, activity is a measure of the “effective conc.” of a species in a mixture.

That means that the species' chemical potential depends on its activity in a real solution in the same way that it would depend on its conc. in an ideal solution.

Can you please simplify the concept by drawing an analogy?

To paint a wall you would need labors.

The following is a table that shows the relationship between the number of labors and the time consumed to paint the wall.

No of Labors	Time, hours	Effective No of Manpower
1	8	1
2	4	2
4	2.5	3.2
8	1.6	5

Ref: Wikipedia.org,
Smith & Van Ness

- The species' chemical potential (μ_i) depends on its activity in a real solution in the same way that it would depend on its conc. in an ideal solution.
- By convention, activity is treated as a dimensionless quantity, although its actual value depends on customary choices of standard state for the species.
- The difference between activity and other measures of composition (e.g. conc.) arises because molecules in non-ideal solutions interact with each other, either to attract or to repel each other.
- Activities should be used to define equilibrium constants but, in practice, concentrations are often used instead. The same is often true of equations for reaction rates.
- However, there are circumstances where the activity & conc. are significantly different and, as such, it is not valid to approximate with conc. where activities are required.

Back to

$$\prod_i \left(\hat{f}_i / f_i^\circ \right)^{\nu_i} = \exp \left(\frac{-\Delta G^\circ(T)}{RT} \right)$$

The term $\exp \left(\frac{-\Delta G^\circ}{RT} \right)$ is given the symbol K , and is called the

equilibrium constant for the rxn, and is function of temperature **ONLY**:

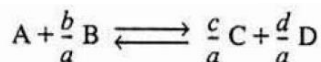
$$K \equiv \exp \left(\frac{-\Delta G^\circ(T)}{RT} \right)$$

$$\square \text{ Therefore, } \prod_i \left(\hat{f}_i / f_i^\circ \right)^{\nu_i} = K \quad \therefore a_i \equiv \hat{f}_i / f_i^\circ$$

$$\therefore \prod_i (a_i)^{\nu_i} = K, \text{ where } a_i \text{ is the activity (effective concentration)}$$

of species i & ν_i is its stoichiometric number.

For the reaction:



1. The true (dimensionless) equilibrium constant

$$K = \frac{a_C^{c/a} a_D^{d/a}}{a_A a_B^{b/a}}$$

$$K = \prod_i (a_i)^{\nu_i}$$

K = True equilibrium constant

K_p = Pressure equilibrium constant
 K_c = Concentration equilibrium constant

2. The pressure equilibrium constant K_p is

$$K_p = \frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}}$$

$$K_p = \prod_i (P_i)^{\nu_i}$$

3. The concentration equilibrium constant K_C is

$$K_C = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}}$$

$$K_c = \prod_i (C_i)^{\nu_i}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

(A) Equilibrium Constant (K) for Gas-Phase Reactions:

f_i° is the standard state fugacity.

The standard state for a gas is the ideal-gas state of the pure gas at the standard-state pressure P° of 1 bar.

Because the fugacity of an ideal gas is equal to its P , $f_i^\circ = P^\circ = 1 \text{ bar}$.

$\hat{f}_i$ is the fugacity of species i in the gas mixture.

The fugacity is related to the fugacity coefficient by: $\hat{\phi}_i = \hat{f}_i / P_i$

or $\hat{f}_i = \hat{\phi}_i P_i = \hat{\phi}_i y_i P$

Therefore, for gases: $a_i = \hat{f}_i / f_i^\circ = \hat{\phi}_i P_i / P^\circ$

$$K = \prod_i (a_i)^{\nu_i} = \prod_i (\hat{\phi}_i P_i / P^\circ)^{\nu_i}$$

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^\circ)^{-\nu_i}$$

$\hat{\phi}_i$ is a measure of deviation from ideal-gas (ig) behavior for gaseous mixtures:

$$\hat{\phi}_i \equiv \hat{f}_i / P_i$$

$$\hat{\phi}_i = \hat{f}_i / \hat{f}_i^{ig}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

(A) Equilibrium Constant (K) for Gas-Phase Reactions:

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^\circ)^{-\nu_i} \quad \left| \begin{array}{l} \text{where,} \\ K_\phi \equiv \prod_i (\hat{\phi}_i)^{\nu_i} \\ K_p \equiv \prod_i (P_i)^{\nu_i} \end{array} \right.$$

$$K = K_\phi \cdot K_p \cdot (P^\circ)^{-\delta}$$

For ideal gases (high T , low P):

$$1. \hat{\phi}_i = 1 \quad \therefore K_\phi = 1 \quad \& \quad K = K_p \cdot (P^\circ)^{-\delta} \quad \left| \begin{array}{l} \delta \equiv \sum_i \nu_i \end{array} \right.$$

$$2. P_i = C_i RT$$

$$\therefore K_p = \prod_i (C_i RT)^{\nu_i} = (RT)^\delta \cdot \prod_i (C_i)^{\nu_i} \quad \left| \begin{array}{l} \text{where,} \\ K_c \equiv \prod_i (C_i)^{\nu_i} \end{array} \right.$$

$$K_p = (RT)^\delta \cdot K_c \quad \Rightarrow \quad K = K_c \cdot (RT / P^\circ)^\delta$$

For reactions between ideal gases with no change in the total number of moles ($\delta=0$): $K = K_p = K_c$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

(B) Equilibrium Constant (K) for Liquid-Phase Reactions:

f_i° is the standard state fugacity.

For liquids, f_i° is the fugacity of pure liquid i at the system T and 1 bar.

$\hat{f}_i$ is the fugacity of species i in the solution.

The fugacity is related to the activity coefficient by: $\hat{f}_i = \gamma_i x_i f_i$

where f_i is fugacity of pure liquid i at system T & P .

Therefore, for liquid solution:

$$a_i = \hat{f}_i / f_i^\circ = \gamma_i x_i f_i / f_i^\circ = \gamma_i x_i (f_i / f_i^\circ)$$

Because the fugacities of liquids are weak functions of P , the ratio f_i / f_i° is often taken as unity.

$$\therefore a_i = \hat{f}_i / f_i^\circ \cong \gamma_i x_i$$

γ_i is a measure of deviation from ideal-solution (id) behavior for liquid solutions:

$$\gamma_i \equiv \hat{f}_i / x_i f_i$$

$$\gamma_i = \hat{f}_i / \hat{f}_i^{id}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0 = \gamma_i x_i$$

(B) Equilibrium Constant (K) for Liquid-Phase Reactions:

$$\begin{aligned} K &= \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i (\gamma_i C_i / C_T)^{\nu_i} \\ K &= \prod_i (\gamma_i)^{\nu_i} \prod_i (C_i)^{\nu_i} \prod_i (C_T)^{-\nu_i} \\ K &= K_\gamma \cdot K_c \cdot (C_T)^{-\delta} \end{aligned} \quad \left| \begin{array}{l} \text{where,} \\ K_\gamma \equiv \prod_i (\gamma_i)^{\nu_i} \\ K_c \equiv \prod_i (C_i)^{\nu_i} \\ \delta \equiv \sum_i \nu_i \end{array} \right.$$

For ideal solutions (molecular species are similar in size & chemical nature): $\gamma_i = 1 \quad \therefore K_\gamma = 1$

$$K = K_c \cdot (C_T)^{-\delta}$$

For reactions occurring in ideal solution with no change in the total number of moles ($\delta=0$): $K = K_c$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0$$

In Summary:

$$\begin{aligned} \text{1. For Gas Phase RXNs: } K &= K_\phi \cdot K_p \cdot (P^0)^{-\delta} \\ \text{For ideal gases:} \\ K &= K_p \cdot (P^0)^{-\delta} \\ K &= K_c \cdot (RT / P^0)^{\delta} \end{aligned} \quad \left| \begin{array}{l} \text{where,} \\ K_\phi = \prod_i (\hat{\phi}_i)^{\nu_i} \\ K_p = \prod_i (P_i)^{\nu_i} \\ K_c = \prod_i (C_i)^{\nu_i} \\ \delta = \sum_i \nu_i \end{array} \right.$$

$$\text{2. For Liquid Phase RXNs: } K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta}$$

For ideal solutions:

$$K = K_c \cdot (C_T)^{-\delta}$$

The effect of Temperature on the Equilibrium Constant:

- Recall Van't Hoff's equation: $\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^o(T)}{RT^2}$
- If heat capacities, C_p , can be assumed constant or its average values can be used, ΔH_{rxn} can be written as:

$$\Delta H_{rxn}^o(T) = \Delta H_{rxn}^o(T_R) + \Delta C_p(T - T_R)$$

$$\therefore \frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^o(T_R) + \Delta C_p(T - T_R)}{RT^2}$$

- Upon integration:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^o(T_R) - T_R \Delta C_p}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T_2}{T_1} \right)$$

The effect of Temperature on the Equilibrium Constant:

- Back to Van't Hoff's equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^o(T)}{RT^2}$$

- If ΔH^o , the standard heat of rxn, is assumed independent of T (reasonable assumption over small T range), integration of the above Eq. leads:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Special Case 1: Ideal Gas with Constant ΔH_{rxn} :

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

□ For ideal gases:
$$\frac{K(T_2)}{K(T_1)} = \frac{K_p(T_2) \cdot (P^o)^{-\delta}}{K_p(T_1) \cdot (P^o)^{-\delta}} = \frac{K_p(T_2)}{K_p(T_1)}$$

□ Therefore, for ideal gas reaction mixture with constant ΔH_{rxn} :

$$K_p(T_2) = K_p(T_1) \exp \left[\frac{-\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

□ and when there is no change in the total number of moles ($\delta=0$),
 $K = K_p = K_c$:

$$K_c(T_2) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

Special Case 2: Ideal Liquid Solution with Constant ΔH_{rxn} & $\delta = 0$

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

□ For ideal liquid solutions:

$$K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta} \Rightarrow K = K_c \cdot (C_T)^{-\delta}$$

□ For cases where $\delta = 0$, $K = K_c$

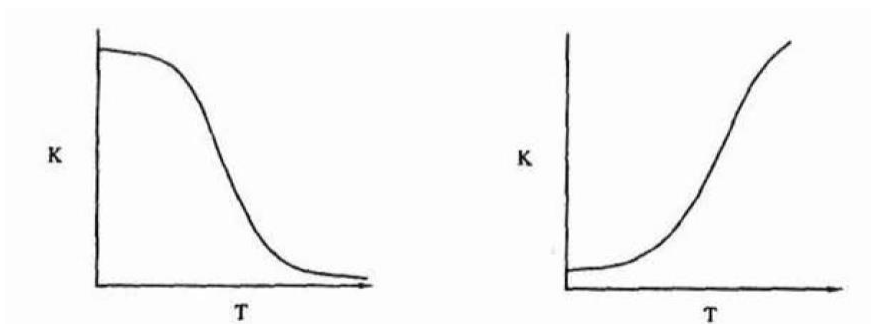
□ Therefore, for ideal liquid solutions with constant ΔH_{rxn} & $\delta = 0$:

$$\ln \frac{K_c(T_2)}{K_c(T_1)} = -\frac{\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_c(T_2) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

Quick test:

- Classify these rxns into exothermic or endothermic:



Reaction 1

Reaction 2

Exothermic

Endothermic

The following conclusions may be drawn from thermodynamics:

1. If you have the value of the thermodynamic equilibrium constant (K), you can calculate the value of the concentration equilibrium constant (K_c).
2. K is unaffected by the P of the system, by the presence or absence of inerts, or by the kinetics of the rxn, but is affected by the T of the system.
3. i.e. $K = f(T)$ only & its value for a given rxn can be found by thermodynamic calculations or from thermodynamic charts.
4. Though K is unaffected by P or inerts, the equilibrium concentrations & X_e can be influenced by these variables.
5. $K \gg 1$ indicates that: practically complete conversion may be possible & that the rxn can be considered to be irreversible.
6. $K \ll 1$ indicates that: reaction will not proceed to any appreciable extent.

The following conclusions may be drawn from thermodynamics:

6. K_c decreases with increasing T for exothermic rxns and increases with increasing T for endothermic rxns.
7. For an increase in T , X_e rises for endothermic rxns and drops for exothermic rxns.
8. For an increase in P in gas phase rxns:
 X_e rises when the no. of moles decreases with rxn (e.g. $2A \leftrightarrow B$) and X_e drops when the no. of moles increases with rxn (e.g. $A \leftrightarrow 2B$).
9. For a decrease in inerts for all rxns,
 X_e rises when the no. of moles decreases with rxn (e.g. $2A \leftrightarrow B$) and X_e drops when the no. of moles increases with rxn (e.g. $A \leftrightarrow 2B$).



Back to Chemical Reaction Engineering

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