Physical Chemistry
Chapter 5
PRINCIPLES OF CHEMICAL EQUILIBRIUM

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Chapter Description

- Aims
  - To understand the fundamental of reaction Gibbs Energy
  - To understand reactions at equilibrium state
  - To understand the response of equilibrium in the presence of catalyst

- Expected Outcomes
  - Student will be able to determine the reaction Gibbs Energy
  - Student will be able to explain reaction at equilibrium state

- Other related Information

  <u>Problem Analysis</u> - Identify, formulate, research literature and analyse complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences and engineering sciences.

Contents

- The Reaction Gibbs Energy
- Reactions at Equilibrium
- The Standard Reaction Gibbs energy
- The Response of Equilibrium to the conditions (presence of catalyst,
- Temperature and compression)

INTRODUCTION

- The thermodynamic criterion for spontaneous change at constant T and P is $\Delta G<0$.
- Therefore, at constant T and P, a reaction mixture tends to adjust its composition until its Gibbs energy at minimum.

The Reaction Gibbs Energy

THE REACTION GIBBS ENERGY, $\Delta_r G$

Two ways to interpret $\Delta_r G$:

- The difference of chemical potential of products and reactants.
- The change in Gibbs energy, ΔG divided by the change in composition. (Fig 1).

THE REACTION GIBBS ENERGY, $\Delta_r G$

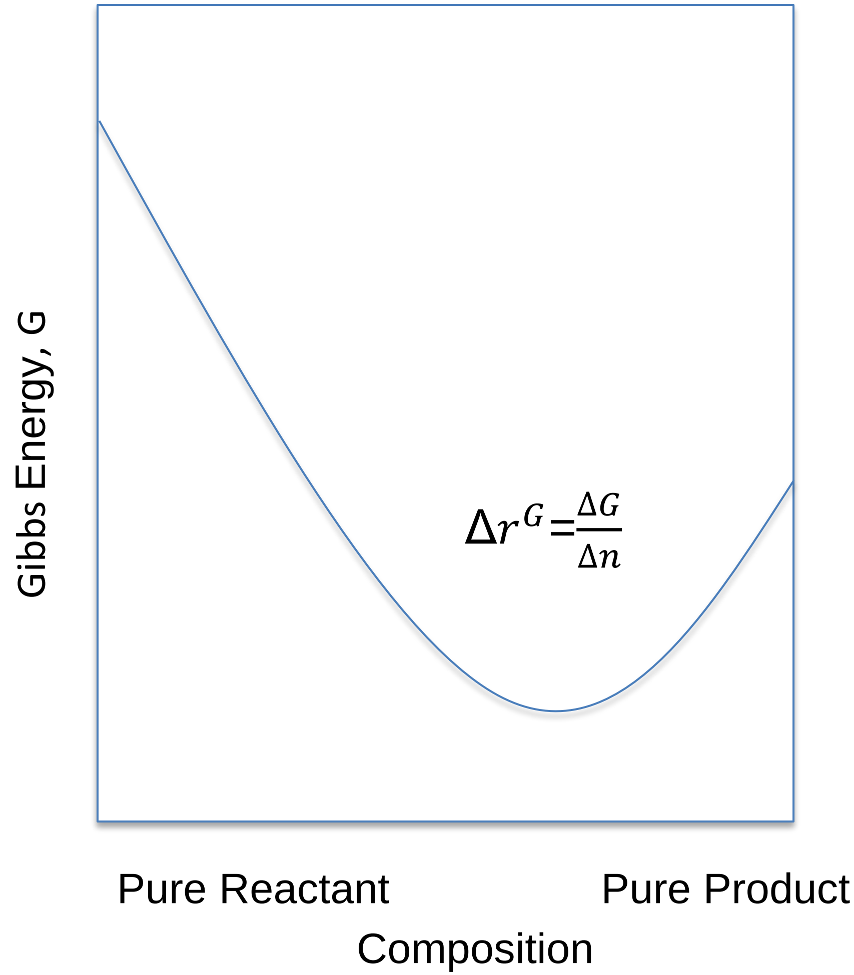


Figure 1: Reaction Gibbs Energy vs composition changes

THE REACTION GIBBS ENERGY

- A general chemical reaction is given by

$$aA + bB \rightarrow cC + dD$$

- note that each chemical potential is multiplied by the corresponding stoichiometric coefficient and that reactants are substracted from products

$$\Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A - b\mu_B)$$

- Note that for the reaction

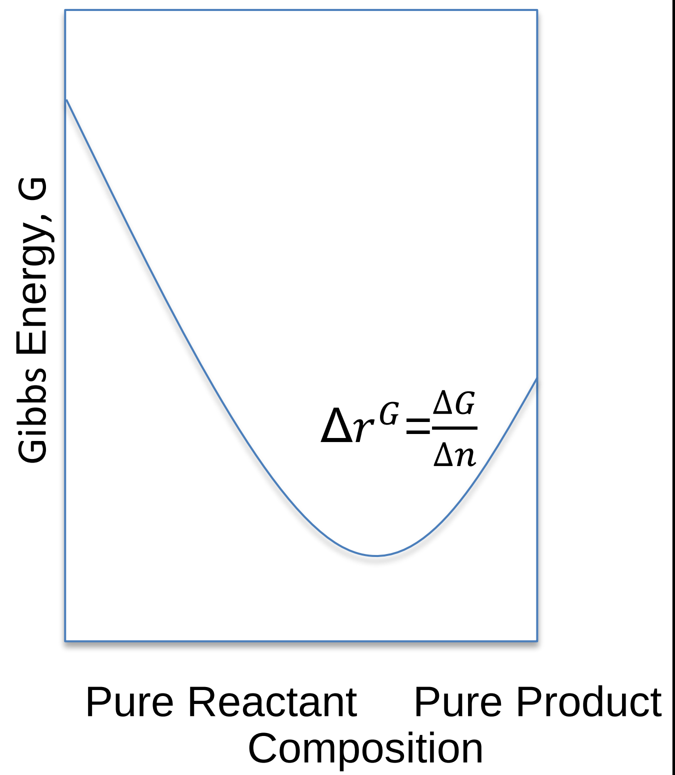
$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$\Delta G = \left(\mu_{NH_3} \times 2\Delta n\right) - \left(\mu_{N_2} \times \Delta n\right) - \left(\mu_{H_2} \times 3\Delta n\right)$$
$$= \left(2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}\right)\Delta n$$

$$\Delta_r G = \frac{\Delta G}{\Delta n} = \left(2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}\right)$$

Discussion on Figure 1

- Chemical potential depends on
  - Concentration of mixtures
  - Partial pressure
- $\Delta G_r < 0$ when the mixture is rich in the reactants; tends to form more products
- $\Delta G_r > 0$ when the mixture is rich in the products; the reverse reaction is spontaneous and the products tend to decompose into reactants.



The Standard Reaction Gibbs Energy

Determine the standard reaction Gibbs energy, $\Delta_r G^o$ from standard reaction enthalpy, $\Delta_r H^o$ and standard reaction entropy, $\Delta_r S^o$ using equation

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

- Determine Gibbs energy from the list of **standard Gibbs energy of formation**.

$$\Delta_r G^o = \sum v\Delta_f G^o(products) - \sum v\Delta_f G^o(reactants)$$

The response of equilibrium to catalyst, temperature and compression

Le Chatelier's Principle

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- When a system at equilibrium is subjected to a disturbance, the composition of the systems adjusts so as to tend to minimize the effect of the disturbance.

Conclusion of The Chapter

- Conclusion
  - Le Chatelier's principle perfectly explains the observations of the shifts in equilibrium of the reaction as the system was subjected to various stresses.
  - When the temperature was increased, the system shifted right to favor the products and when the temperature was decreased, it shifted left to favor the reactants.

Author Information

Credit to authors: Dr Suriati Ghazali, Dr Sunarti Abd Rahman, Dr Norhayati Abdullah, Dr Izirwan Izhab