

CHEM 3410: Physical Chemistry I — Fall 2008

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Lecture 16: Chemical equilibrium and  $K_p$

## References

1. Levine, *Physical Chemistry*, Sections 6.1–6.4

## Key Concepts

- We defined  $\xi$  as the extent of reaction, or that a reaction advances in the forward direction by  $\xi$  moles. By doing this we can determine what direction we would expect to see change or if the reaction is at equilibrium.

$$dG_{rxn} = \sum \mu_i dn_i = \sum \mu_i \nu_i d\xi$$

where  $\nu_i$  represents the stoichiometric coefficients in the reaction. At equilibrium,  $dG_{rxn} = 0$ .

- We were able to arrive at the following relation at equilibrium, for example for the gas-phase reaction of  $aA + bB \rightarrow cC + dD$ :

$$\Delta \bar{G}_{rxn}^{\circ} = -RT \ln \frac{\left(\frac{P_C}{P^{\circ}}\right)^c \left(\frac{P_D}{P^{\circ}}\right)^d}{\left(\frac{P_A}{P^{\circ}}\right)^a \left(\frac{P_B}{P^{\circ}}\right)^b} = -RT \ln K_p$$

- For the generic gas-phase reaction:  $aA + bB \rightarrow cC + dD$ , we can write the following relationship for  $\Delta \bar{G}_{rxn}$ :

$$\Delta \bar{G}_{rxn} = \Delta \bar{G}_{rxn}^{\circ} + RT \ln Q_p$$

where  $\Delta \bar{G}_{rxn}^{\circ}$  is the free energy of the reaction with all the participants in their standard states and  $Q_p$  is the reaction quotient:

$$Q_p = \frac{\left(\frac{P_C}{P^{\circ}}\right)^c \left(\frac{P_D}{P^{\circ}}\right)^d}{\left(\frac{P_A}{P^{\circ}}\right)^a \left(\frac{P_B}{P^{\circ}}\right)^b}$$

This expression is true at any point during a reaction. If you insert the current values of the partial pressures into the expression for  $Q$ ,  $\Delta \bar{G}_{rxn}$  can be determined.

- If  $\Delta \bar{G}_{rxn} < 0$  the products are at a lower energy as compared to the reactants and the reaction will spontaneously proceed forward. If  $\Delta \bar{G}_{rxn} > 0$ , the reactants are at a lower free energy compared to the products, meaning the reaction will spontaneously proceed in reverse.
- At equilibrium,  $\Delta \bar{G}_{rxn} = 0$  and  $Q_p = K_p$ , where  $K_p$  is the equilibrium constant:

$$0 = \Delta \bar{G}_{rxn}^{\circ} + RT \ln K_p$$

$$\Delta \bar{G}_{rxn}^{\circ} = -RT \ln K_p$$

- If  $\Delta \bar{G}_{rxn}^{\circ} < 0$ , then  $K_p > 1$  and the products are favored at equilibrium. If  $K_p$  is very large, we usually say that these reactions go to completion.
- If  $\Delta \bar{G}_{rxn}^{\circ} > 0$ , then  $K_p < 1$  and the reactants are favored at equilibrium.
- The equilibrium constant,  $K_p$ , is a function of temperature but not of total pressure:  $K_p(T)$ . If we assume that the standard enthalpy of the reaction ( $\Delta \bar{H}_{rxn}^{\circ}$ ) is independent of temperature, then we can arrive at the following expression for the temperature dependence of  $K_p$ :

$$\ln K_p(T_2) = \ln K_p(T_1) + \frac{\Delta \bar{H}_{rxn}^{\circ}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

This gives a quantitative representation of Le Chatelier's principle regarding the response of a system at equilibrium to changes in temperature.