

CHEM 3410: Physical Chemistry I — Fall 2008

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Lecture 16: Chemical Reactions

### References

1. Levine, *Physical Chemistry*, Sections 4.6–4.8, 6.1–6.2

### Key Concepts

- Based on our expression for the chemical potential of an ideal gas in a mixture, we were able to arrive at an expression for the free energy of mixing of ideal gases. In general for a system of  $i$  gases and then for a two-component system (A & B) we wrote:

$$\Delta\bar{G}_{mix} = RT \sum X_i \ln X_i$$

$$\Delta\bar{G}_{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

- We can find the entropy of mixing since  $-S = \left(\frac{\partial G}{\partial T}\right)_P$ :

$$\Delta\bar{S}_{mix} = -\left(\frac{\partial\Delta\bar{G}_{mix}}{\partial T}\right)_P = -R \sum X_i \ln X_i$$

So the entropy of mixing of ideal gases is always positive, which is expected.

- In general, for any other phase we will write the chemical potential as a function of  $T$ ,  $P$ , and composition through the introduction of the activity,  $a_i$ :

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

We do this because we would like apply the same form for  $\mu$  that we arrived at for ideal gases to other types of substance. We have just transferred our ignorance of how  $\mu$  behaves to this quantity we call the activity.

- We further transfer our ignorance by relating the activity to the composition of the system through the activity coefficient,  $\gamma_i$ :

$$a_i = \gamma_i X_i$$

All of the chemistry, that is any interactions between species  $i$  and the other components is captured in the activity coefficient. You can see when  $\gamma_i = 1$ , this reduces to the same expression we had for the chemical potential of an ideal gas in a mixture.

- For a positive deviation from ideality, the chemical potential (and activity) of a component is greater than predict in the ideal case. This means that repulsive interactions are dominating since mixing the two component raises the chemical potential, i.e. makes it less stable.
- For a negative deviation from ideality attractive forces dominate, making the chemical potential of a component in the mixture less than predict in the ideal case. This means the solution or mixed state is more stable than in the ideal case.
- 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.