

Figure 3-1
Atkins Physical Chemistry, Eighth Edition
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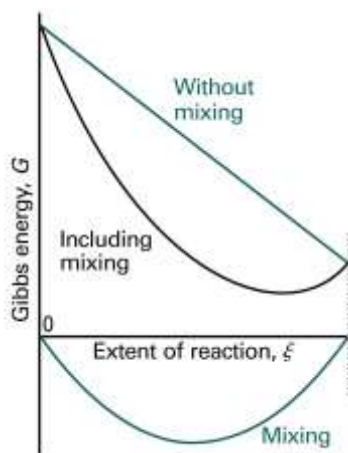
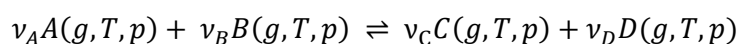


Figure 3-2
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At any time during the course of a reaction, how do we know the composition? (I.G. case)

A general case:



Partial pressures,

$$p_A = X_A p; \quad p_B = X_B p; \quad p_C = X_C p; \quad p_D = X_D p;$$

Is the mixture at equilibrium? Allow the reaction to proceed and see the ΔG .

$$G = \sum_i n_i \mu_i$$

For a small change in the reaction at conditions of (g, T, p) ,

$$\Delta G(\epsilon) = \epsilon [(v_C \mu_C + v_D \mu_D) - (v_A \mu_A + v_B \mu_B)]$$

We know that $\mu_i(g, T, p) = \mu_i^0(T) + RT \ln p_i$, which gives,

$$\Delta G(\epsilon) = \epsilon \left[\{v_C \mu_C^0(T) + v_D \mu_D^0(T)\} - \{v_A \mu_A^0(T) + v_B \mu_B^0(T)\} + RT \ln \left(\frac{p_C^{v_C} p_D^{v_D}}{p_A^{v_A} p_B^{v_B}} \right) \right]$$

$$\Delta G = \Delta G^0 + RT \ln Q \quad (\text{taking } \epsilon = 1)$$

ΔG^0 is the standard free energy change for taking pure reactants to pure products.

At equilibrium, $\Delta G(\epsilon) = 0 \rightarrow \Delta G_{rxn}^0 = -RT \ln K_p$

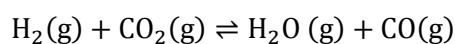
$$K_p = e^{-\Delta G^0/RT}$$

So, $K_p(T)$ is not a function of p .

$$k_p = \left(\frac{p_C^{v_C} p_D^{v_D}}{p_A^{v_A} p_B^{v_B}} \right)_{eq} = p^{\Delta v} \left(\frac{X_C^{v_C} X_D^{v_D}}{X_A^{v_A} X_B^{v_B}} \right)_{eq} = p^{\Delta v} K_X$$

But $K_X = p^{-\Delta v} K_p$ is a function of p, T i.e. $K_X(p, T)$. All equilibrium constants are unitless.

Examples

Example 1

$$T = 298 \text{ K}, p = 1 \text{ bar}$$

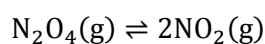
| | | | | |
|--|-------------------|-------------------|-----------------|-----------------|
| Initial number of moles | a | b | 0 | 0 |
| number of moles at eq. | $a - x$ | $b - x$ | x | x |
| mole fractions | $\frac{a-x}{a+b}$ | $\frac{b-x}{a+b}$ | $\frac{x}{a+b}$ | $\frac{x}{a+b}$ |
| ΔG_f° (kJ mol ⁻¹) | 0 | -396.6 | -228.6 | -137.2 |

$$\text{So, } \Delta G_{rxn}^\circ = 28.6 \text{ kJ mol}^{-1} \Rightarrow K_p = \exp -28600 \text{ J} \frac{\text{mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = e^{-11.54} = 9.7 \times 10^{-6}$$

$$K_p = \frac{p_{\text{H}_2\text{O}} p_{\text{CO}}}{p_{\text{H}_2} p_{\text{CO}_2}} = \frac{X_{\text{H}_2\text{O}} X_{\text{CO}}}{X_{\text{H}_2} X_{\text{CO}_2}} = \frac{x^2}{(a-x)(b-x)} = 9.7 \times 10^{-6}$$

Take, $a = 1 \text{ mol}, b = 2 \text{ mol},$

Since $K \ll 1, x \ll 1 \Rightarrow 1 - x \sim 1, 2 - x \sim 2 \therefore x \sim 0.0044 \text{ mol}$

Example 2

Initial mol: $n \quad 0$

At eq : $n-x \quad 2x$

X_i 's at eq. : $\frac{n-x}{n+x} \quad \frac{2x}{n+x}$

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{p^2 X_{\text{NO}_2}^2}{p X_{\text{N}_2\text{O}_4}} = \frac{p \left(\frac{2x}{n+x} \right)^2}{\left(\frac{n-x}{n+x} \right)} = p \frac{4x^2}{n^2 - x^2} = p \frac{4\alpha^2}{1 - \alpha^2}$$

If $\alpha = x/n$ is the fraction reacted, $\alpha = \left(1 + \frac{4p}{K_p} \right)^{-1/2}$

If p increases, α decreases \rightarrow Le Chatelier's for pressure