Lecture 17

Thursday, November 9, 2023 11:29

6A Chemical Equilibrium continued

$$K = \left(\prod_J a_J^{\nu_J} \right)_{\text{equilibrium}}$$

Degree of dissociation at equilibrium

α : fraction of reactant that has decomposed

initial : n

equilibrium : n_{eq}

$$\alpha = \frac{n - n_{eq}}{n}$$

$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2} O_2(g)$$

$T = 2300\ K$

$\Delta_r G^{\circ} = +118.08\ kJ \cdot mol^{-1}$

What is the degree of dissociation of H_2O at equilibrium, with a total pressure of 1.00 bar?

Step 1: find K.

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$= \frac{-1.1808 \times 10^5\ \cancel{J} \cdot \cancel{mol^{-1}}}{8.3145\ \cancel{J} \cdot \cancel{K^{-1}} \cdot \cancel{mol^{-1}} \times 2300\ \cancel{K}}$$

$$\ln K = -6.17$$

$$\boxed{K = 2.08 \times 10^{-3}}$$

Step 2: find α

	$H_2O \rightarrow$	H_2	$+\ \frac{1}{2}O_2$
Initial amount	n	0	0
Change to reach equilibrium	$-\alpha n$	$+\alpha n$	$+\frac{1}{2}\alpha n$
Amount at equilibrium	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
			Total: $(1+\frac{1}{2}\alpha)n$

Mole fraction, x_J	$\frac{(1-\alpha)\cancel{n}}{(1+\frac{1}{2}\alpha)\cancel{n}}$	$\frac{\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Partial pressure, p_J	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

$$p_J = x_J p$$

$$p_{H_2O} = \frac{2(1-\alpha)p}{2+\alpha}$$

$$\boxed{K = \frac{p_{H_2}\, p_{O_2}^{1/2}}{p_{H_2O}}}$$

$$p_{H_2} = \frac{2\alpha p}{2+\alpha}$$

$$p_{O_2} = \frac{\alpha p}{2+\alpha}$$

(simplified using p_J instead $p_J/p^{\ominus}$)

$$\frac{\cancel{2}\alpha p/\cancel{(2+\alpha)}\cdot[\alpha p/(2+\alpha)]^{1/2}}{\cancel{2}(1-\alpha)p/\cancel{(2+\alpha)}}$$

$$= \frac{\alpha^{3/2}\, p^{\cancel{3}/2}}{(1-\alpha)\cancel{p}\,(2+\alpha)^{1/2}}$$

$$\boxed{K = \frac{\alpha^{3/2}\, p^{1/2}}{\underline{(1-\alpha)}\,\underline{(2+\alpha)}^{1/2}}}$$

because $K \ll 1$

$\alpha \ll 1$

2

using approximation:

$$K = \frac{\alpha^{3/2}\, p^{1/2}}{2^{1/2}}$$

$$\alpha = \left(\frac{2^{1/2} K}{p^{1/2}}\right)^{2/3}$$

implicitly divided by $p^{\ominus}$

$$\alpha = \left(\frac{2^{1/2} \cdot 2.08 \times 10^{-3}}{(1.00)^{1/2}}\right)^{2/3}$$

$$\boxed{\alpha = 0.0205}$$

about 2% of water has decomposed

Topic 6B: The Response of Equilibria to the Conditions

$$A(g) \rightleftharpoons 2B(g)$$

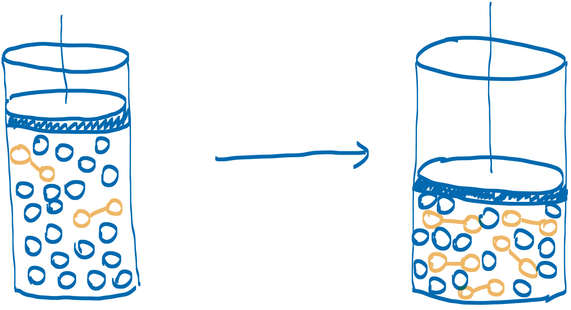
$$K = \frac{(p_B/p^{\ominus})^2}{p_A/p^{\ominus}} = \boxed{\frac{p_B^2}{p_A\, p^{\ominus}}}$$

What happens when total pressure is increased? (E.g. decrease the volume of the container)

To keep the ratio constant, an increase in p_A has to balance the square of an increase in P_B. Thus, equilibrium will shift toward A.

A system at equilibrium, when subjected to a disturbance, tends to respond in a way that minimizes the effect of the disturbance.

—Le Chatelier's Principle



$A(g) \rightleftharpoons 2B(g)$ $A(g) \leftharpoons 2B(g)$

Suppose we have n amount of A present initially, and no B

	A	B
initial	n	0
equilibrium	$(1-\alpha)n$	$2\alpha n$

$$x_A = \frac{n_A}{n_{tot}} = \frac{(1-\alpha)\cancel{n}}{(1-\alpha)\cancel{n}+2\alpha\cancel{n}}$$

$$= \frac{1-\alpha}{1-\alpha+2\alpha}$$

$$\boxed{x_A = \frac{1-\alpha}{1+\alpha}}$$

$$x_B = \frac{n_B}{n_{tot}} = \frac{2\alpha\cancel{n}}{(1-\alpha)\cancel{n}+2\alpha\cancel{n}}$$

$$\boxed{x_B = \frac{2\alpha}{1+\alpha}}$$

$p_J = x_J p$

$$K = \frac{p_B^2}{p_A p^\ominus} = \frac{(x_B p)^2}{x_A p \cdot p^\ominus}$$

$$K = \frac{x_B^2 p^{\cancel{2}}}{x_A \cancel{p} \cdot p^\ominus}$$

$$= \frac{(2\alpha)^2/(1+\alpha)^{\cancel{2}} \cdot p}{(1-\alpha)/\cancel{(1+\alpha)} \cdot p^\ominus}$$

$$= \frac{4\alpha^2 \cdot p/p^\ominus}{(1-\alpha)(1+\alpha)}$$

$$\boxed{K = \frac{4\alpha^2 \cdot (p/p^\ominus)}{1-\alpha^2}}$$

$$K(1-\alpha^2) = 4\alpha^2 \cdot (p/p^\ominus)$$

$$K - K\alpha^2 = 4\alpha^2 \cdot (p/p^\ominus)$$

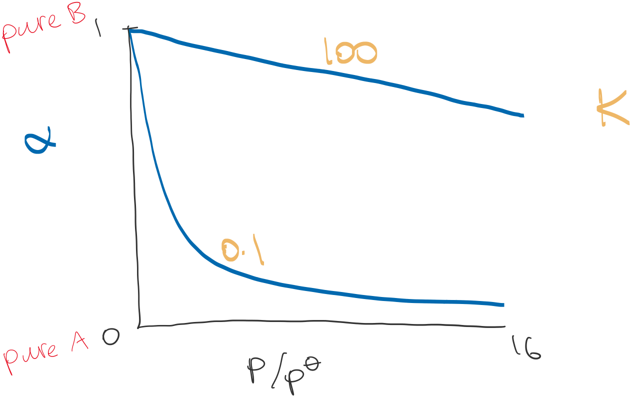
$$K = 4\alpha^2 \cdot (p/p^\ominus) + K\alpha^2$$

$$K = \alpha^2 \left[4(p/p^\ominus) + K \right]$$

$$\alpha^2 = \frac{K}{4(p/p^\ominus) + K}$$

$$\boxed{\alpha = \left(\frac{1}{1 + 4p/Kp^\ominus} \right)^{1/2}}$$

- K is independent of pressure
- however, amounts of A and B at equilibrium do depend on pressure
- as p increases, α decreases



The Response to Temperature

Exothermic reactions: increased temperature favours the reactants

Endothermic reactions: increased temperature favours the products

Derive an expression for the variation of ln K with temperature.

$$\Delta_r G^{\ominus} = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT}$$

Differentiate with respect to temperature:

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^{\ominus}/T)}{dT}$$

$$\boxed{-R\frac{d\ln K}{dT} = \frac{d(\Delta_r G^\ominus/T)}{dT}}$$

$\Delta_r G^\ominus$ and K depend only on temperature, not pressure

Use Gibbs–Helmholtz equation:

$$\boxed{\frac{d(G/T)}{dT} = -\frac{H}{T^2}}$$

$$\cancel{-}R\frac{d\ln K}{dT} = \cancel{-}\frac{\Delta_r H^\ominus}{T^2}$$

$$R\frac{d\ln K}{dT} = \frac{\Delta_r H^\ominus}{T^2}$$

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}}$$

Van't Hoff equation

$\Delta_r H^\ominus < 0$: exothermic reaction

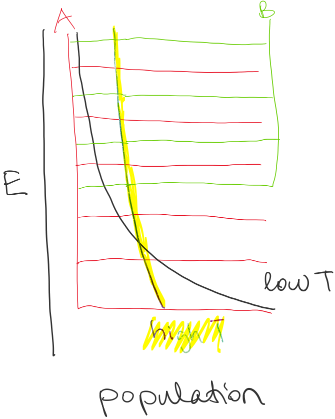
$$\frac{d\ln K}{dT} < 0, \text{ i.e. } \frac{dK}{dT} < 0$$

K decreases with temperature

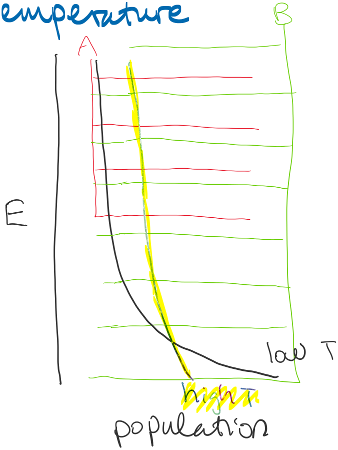
$\Delta_r H^\ominus > 0$: endothermic reaction

$$\frac{d\ln K}{dT} > 0, \text{ i.e. } \frac{dK}{dT} > 0$$

K increase with temperature



population of B increases at the expense of A



population of A increases at the expense of B