# Lecture 21

Thursday, November 23, 2023 11:29

## CHEM*2820 Problem-Solving Review

1. The reaction $A \rightleftharpoons B$ is first order in both directions.

a) Derive an expression for the concentration of A as a function of time when the initial molar concentrations of A and B are $[A]_0$ and $[B]_0$.

b) What is the final composition of the system?

**Solution:**

a) $A \xrightarrow{k_f} B \qquad \frac{d[A]}{dt} = -k_f[A]$

$B \xrightarrow{k_r} A \qquad \frac{d[A]}{dt} = +k_r[B]$

$$\frac{d[A]}{dt} = -k_f[A] + \underbrace{k_r[B]}_{}$$

need an expression in terms of [A]

| $t$ | $[A]$ | $[B]$ |
|---|---|---|
| $0$ | $[A]_0$ | $[B]_0$ |
| $t'$ | $[A]$ | $\boxed{[B]_0 + ([A]_0 - [A])}$ |

$$\frac{d[A]}{dt} = -k_f[A] + k_r\{[B]_0 + ([A]_0 - [A])\}$$

$$\frac{1}{-k_f[A] + k_r\{[B]_0 + ([A]_0 - [A])\}}\, d[A] = dt$$

$$\frac{1}{-k_f[A] - k_r[A] + k_r([B]_0 + [A]_0)}\, d[A]$$

$$\frac{1}{k_r([B]_0 + [A]_0) - (k_f + k_r)[A]}\, d[A] = dt$$

$$\int \frac{1}{a - bx}\, dx = \ln(a - bx) \cdot \frac{1}{-b}$$

$$\int_{[A]_0}^{[A]} \frac{1}{k_r([B]_0 + [A]_0) - (k_f + k_r)[A]}\, d[A] = \int_0^t dt$$

$$-\ln\left\{k_r([B]_0+[A]_0)-(k_f+k_r)[A]\right\}\frac{1}{(k_f+k_r)}\Bigg|_{[A]_0}^{[A]} = t$$

solve for [A]

$$\ln\frac{k_r([B]_0+[A]_0)-(k_f+k_r)[A]}{k_r([B]_0+[A]_0)-(k_f+k_r)[A]_0} = -(k_f+k_r)t$$

$$\frac{k_r([B]_0+[A]_0)-(k_f+k_r)[A]}{k_r([B]_0+[A]_0)-(k_f+k_r)[A]_0} = e^{-(k_f+k_r)t}$$

$$k_r([B]_0+[A]_0)-(k_f+k_r)[A]$$

$$=\left\{k_r([B]_0+[A]_0)-(k_f+k_r)[A]_0\right\}e^{-(k_f+k_r)t}$$

$$(k_f+k_r)[A] = k_r([B]_0+[A]_0)$$

$$-\left(k_r[B]_0+\cancel{k_r[A]_0}-k_f[A]_0-\cancel{k_r[A]_0}\right)e^{-(k_f+k_r)t}$$

$$\therefore\ \boxed{[A] = \frac{k_r([B]_0+[A]_0)-(k_r[B]_0+k_f[A]_0)e^{-(k_f+k_r)t}}{k_f+k_r}}$$

b) At equilibrium, what is $\boxed{[A]_{eq}}$ and

$[B]_{eq}$ ?

$t \to \infty$

$$[A] = \frac{k_r([B]_0 + [A]_0) - \cancel{(k_r[B]_0 + k_f[A]_0)e^{-(k_f+k_r)t}}}{k_f + k_r}$$

$$\boxed{[A]_{eq} = \frac{k_r([B]_0 + [A]_0)}{k_f + k_r}}$$

$$[B]_{eq} = [B]_0 + ([A]_0 - [A]_{eq})$$

$$= \frac{(k_f + \cancel{k_r)[B]_0} + (k_f + \cancel{k_r)[A]_0} - k_r(\cancel{[B]_0} + \cancel{[A]_0})}{k_f + k_r}$$

$$\boxed{[B]_{eq} = \frac{k_f([B]_0 + [A]_0)}{k_f + k_r}}$$

---

2. The equilibrium constant for the reaction

$$I_2(s) + Br_2(g) \rightleftharpoons 2Br(g)$$

is 0.164 at 25 °C.

a) Calculate $\Delta_r G^\ominus$ for this reaction.

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

$$= -(8.3145\ J \cdot K^{-1} \cdot mol^{-1})$$

$\cdot (298.15\text{ K}) \cdot \ln 0.164)$

$$\boxed{\Delta_r G^\ominus = +4.48\text{ kJ}\cdot\text{mol}^{-1}}$$

b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25°C, respectively. Find the partial pressure of $IBr(g)$ at equilibrium. Assume that all the bromine is in the gaseous form and that the vapour pressure of iodine is negligible.

| | $I_2(s)$ | $Br_2(g)$ | $2IBr(g)$ |
|---|---|---|---|
| Initial | — | $n$ | $0$ |
| Change | — | $-\alpha n$ | $+2\alpha n$ |
| Equilibrium | — | $(1-\alpha)n$ | $+2\alpha n$ |
| Mole fraction | — | $\frac{(1-\alpha)n}{(1-\alpha)n+2\alpha n}$ | $\frac{2\alpha n}{(1-\alpha)n+2\alpha n}$ |
| simplified | — | $\frac{1-\alpha}{1+\alpha}$ | $\frac{2\alpha}{1+\alpha}$ |

| | | | |
|---|---|---|---|
| partial pressure ($p_J = x_J p$) | — | $\frac{(1-\alpha)p}{1+\alpha}$ | $\frac{2\alpha p}{1+\alpha}$ |

$$K = \frac{a_{IBr}^2}{a_{I_2}\, a_{Br_2}} = \frac{(p_{IBr}/p^{\ominus})^2}{p_{Br_2}/p^{\ominus}}$$

$$K = \frac{p_{IBr}^2}{p_{Br_2}\, p^{\ominus}}$$

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

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

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

$$K = \frac{4\alpha^2}{1-\alpha^2} \frac{p}{p^{\ominus}}$$

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

$$\frac{p^{\ominus}}{p}K - \frac{p^{\ominus}}{p}K\alpha^2 = 4\alpha^2$$

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

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

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

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

$$\alpha = \left(\frac{0.164 \cdot 1\ \text{bar}}{4 \cdot 0.164\ \text{atm} \cdot (1.013\ldots\ \text{bar}/1\ \text{atm}) + 0.164 \cdot 1\ \text{bar}}\right)^{\frac{1}{2}}$$

$$\alpha = 0.444$$

$$p_{\text{IBr}} = \frac{2\alpha p}{1+\alpha}$$

$$= \frac{(2)(0.444)(0.164\ \text{atm})}{1+0.444}$$

$$\boxed{p_{\text{IBr}} = 0.101\ \text{atm} \quad \text{or} \quad 0.102\ \text{bar}}$$

---

3. Suppose that $S$ is regarded as a function of $p$ and $T$ so that

$$dS = \boxed{\left(\frac{\partial S}{\partial p}\right)_T} dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

Use

$$\left(\frac{\partial S}{\partial T}\right)_p = \boxed{\frac{C_p}{T}} \leftarrow C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and an appropriate Maxwell relation to show that

$$\boxed{T dS = C_p dT - \alpha T V dp}$$

where α is defined as

$$\alpha = \boxed{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p}$$

Maxwell relation :

$$\left(\frac{\partial S}{\partial p}\right)_T = \boxed{-\left(\frac{\partial V}{\partial T}\right)_p}$$

$$\boxed{dS = -\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{C_p}{T} dT}$$

$$dS = -\frac{V}{V}\frac{T}{\boxed{T}}\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{C_p}{\boxed{T}} dT$$

$$ds = \frac{1}{T}\left[c_p\,dT - \frac{V}{V}\,T\left(\frac{\partial V}{\partial T}\right)_p dp\right]$$

$$T\,ds = c_p\,dT - T\,\overbrace{\frac{V}{V}\left(\frac{\partial V}{\partial T}\right)_p}^{\alpha} dp$$

$$\boxed{T\,ds = c_p\,dT - TV\alpha\,dp}$$