Spring '09 EE 239

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Problem Set 6 Solution

1. **7.1** (a) $\Delta G_r^{\ominus}(T_0) = (2)(-228.6) - (-856.6) = 399.4$

$\Delta H_r^{\ominus} = (2)(-241.8) - (-910.9) = 427.3$

$$K = e^{-\frac{\Delta G_r^{\ominus}(T_0)}{RT_0}} \; e^{\frac{\Delta H_r^{\ominus}}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)}$$

$RT_0 = 2.48$ kJ/mol ; $RT_1 = 11.42$ kJ/mol

$$K = e^{-\frac{399.4}{2.48}} \; e^{\frac{427.3}{2.48} - \frac{427.3}{11.42}} = e^{\frac{27.9}{2.48}} \; e^{-\frac{427.3}{11.42}}$$

$$K = e^{-26.17} = 4.3 \times 10^{-12} \quad //$$

(b) $$\prod_{\text{gas phases}} x_{i,e}^{\alpha_i} = K\left(\frac{p}{p^{\ominus}}\right)^{-\alpha} = K$$

since $\alpha = 2 - 2 = 0$

Let N_{H_2} = # moles H_2 gas ; ξ = reaction extent

Then 2ξ = # moles H_2O in equilibrium

$N - 2\xi$ = # moles H_2 in equilibrium

$$\frac{(2\xi)^2}{(N-2\xi)^2} = K \implies 2\xi = 2.08 \times 10^{-6} N_{H_2} \text{ moles } H_2O$$

$\xi = 1.04 \times 10^{-6} N_{H_2}$ moles SiO_2 reacted

$\bar{N}_{SiO_2} = 6.023 \times 10^{23}\,\xi = 6.26 \times 10^{17} N_{H_2}$ molecules SiO_2 reacted

We require a volume of SiO_2 reacted given by $V_{SiO_2} = 10^{-7}\ cm \times 78.5\ cm^2 = 7.85 \times 10^{-6}\ cm^3$

The number of molecules of SiO_2 that must be reacted is $\bar{N}_{SiO_2} = 2.67 \times 10^{22} \times 7.85 \times 10^{-6}$

$\bar{N}_{SiO_2} = 2.10 \times 10^{17}$ molecules

Hence $N_{H_2} = \dfrac{2.10 \times 10^{17}}{6.26 \times 10^{17}} = 0.335$ moles H_2

$$P_{H_2} V = N_{H_2} R T_1$$

$$P_{H_2} \cdot 10^{-2}\ m^3 = 0.335\ mol \times 11.42 \times 10^3\ \frac{J}{mol}$$

$$P_{H_2} = 3.83 \times 10^5\ \frac{J}{m^3} = 3.83 \times 10^5\ \frac{N}{m^2}$$

$$P_{H_2} = 3.83\ bar$$

2. Problem 7.2a

$$H_f^\circ(CF_x) = H_f^\circ(C) + x\,H_f^\circ(F) - x\,H_{diss}^\circ(CF)$$

$H_f^\circ(C) \rightarrow 716.7$, $H_f^\circ(F) \rightarrow 79.4$, $H_{diss}^\circ(CF) \rightarrow 552$ kJ/mol

$$\therefore \quad H_f^\circ(CF_x) = 716.7 - 472.6\,x \quad \text{kJ/mol}$$

x	$H_f^\circ(CF_x)$ Calculated	$H_f^\circ(CF_x)$ Tabulated
4	-1174	-925
3	-701.1	-467.4, -477
2	-228.1	-194.1
1	244.1	—

3. Problem 7.5 (a) $K_{eq} = \left(\frac{p}{p^\ominus}\right)^{-3/2} = e^{-\frac{\Delta G_{f,m}}{RT}}$

$RT = 2.48$ kJ at STP

$$\left(\frac{p_{F_2}}{p^\ominus_{F_2}}\right)^{-3/2} = e^{\frac{1431}{2.48}} = 10^{250.6} \Rightarrow p_{F_2} = p^\ominus_{F_2} \times 10^{-167.1}$$ (Tiny!)

So almost all F_2 reacts in equilibrium //

$$\left(\frac{p_{Cl_2}}{p^\ominus_{Cl_2}}\right)^{-3/2} = e^{\frac{628.8}{2.48}} = 10^{110.1} \Rightarrow p_{Cl_2} = p^\ominus_{Cl_2} \times 10^{-73.4}$$ (Tiny also!)

So almost all Cl_2 reacts //

(b) $p = p_0 e^{-\frac{\Delta H_{vap,m}}{RT}}$ in equilibrium and $p = 760$ Torr at $T = 453.2$ °K; so $760 = p_0 e^{-\frac{116 \times 10^3}{(8.31)(453.2)}}$ or

$p_0 = 760\, e^{30.8}$ Torr. Hence at 298 °K

$$p = 760\, e^{30.8}\, e^{-\frac{116 \times 10^3}{(8.31)(298)}} = 8.20 \times 10^{-5} \text{ Torr}$$

$n = 3.5 \times 10^{16}\, p = 2.87 \times 10^{12}$ cm^{-3}

$\bar{v} = \left(\frac{8kT}{\pi M}\right)^{1/2} = 2.07 \times 10^4$ cm/sec. $\Rightarrow$

$\Gamma_r = \frac{1}{4} n \bar{v} = 1.49 \times 10^{16}$ ($AlCl_3$ flux emitted by surface)

$ER = \Gamma_r / n_{Al} = 1.49 \times 10^{16} / 6.03 \times 10^{22} = 2.46 \times 10^{-7}$ cm/sec

$ER = 24.6 \times 60$ Å/min $= 1480$ Å/min. // $AlCl_3$

This is small, so one can not etch aluminum at 25°C in a Cl_2 discharge, except at elevated temperatures. Typically, etches are done at around 100°C. For Fl etching

$$p = 760 \exp\left[\frac{531 \times 10^3}{8.31}\left(\frac{1}{1810} - \frac{1}{373}\right)\right] = 6.5 \times 10^{-57}$$ Tiny //

So no hope of etching Al with fluorine.