Answers - problem set 6

(26) $PCl_5\,(g) \rightleftarrows PCl_3\,(g) + Cl_2\,(g)$

$$\Delta_r G^\ominus = 83680 - 14.52\,T \ln T - 72.26\,T$$
$$= a - bT\ln T - cT$$

a). $\rightarrow \Delta_r G^\ominus (T = 450\,k) = 83680 - 14.52 \cdot 450 \ln 450 - 72.26 \cdot 450$
$$= 11.25 \text{ kJ mol}^{-1}$$

$\rightarrow k_p = \exp\left(\dfrac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\dfrac{-11.25 \cdot 10^3}{8.314 \cdot 450}\right) = 0.0495$

$\rightarrow \Delta_r S^\ominus = -\dfrac{\partial(\Delta_r G^\ominus)}{\partial T} = -\left[-b \ln T - \underbrace{bT \cdot \tfrac{1}{T}}_{1} - c\right] =$

$= b \ln T + b + c = 14.52 \ln 450 + 14.52 + 72.26$
$= 175.5 \text{ J k}^{-1} \text{mol}^{-1}$

$\rightarrow \Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus = 11.25 \cdot 10^3 + 450 \cdot 175.5 = 90.2 \text{ kJ mol}^{-1}$

b).

	PCl_5	PCl_3	Cl_2	total
$n_{initial}$	n	0	0	n
n_{eqm}	$n(1-\alpha)$	$n\alpha$	$n\alpha$	$n(1+\alpha)$
x_i	$(1-\alpha)/(1+\alpha)$	$\alpha/(1+\alpha)$	$\alpha/(1+\alpha)$	1
p_i	$[(1-\alpha)/(1+\alpha)]p$	$[\alpha/(1+\alpha)]p$	$[\alpha/(1+\alpha)]p$	p

c). $k_p = \prod_i a_i^{\nu_i} \underset{\text{perf gas}}{=} \prod_i \left(\dfrac{p_i}{p^\ominus}\right)^{\nu_i}$

$$k_p = \frac{(p_{Cl_3}/p^\ominus)(p_{Cl_2}/p^\ominus)}{(p_{Cl_5}/p^\ominus)} = \frac{\left[\frac{\alpha}{(1+\alpha)} \cdot \frac{p}{p^\ominus}\right]\left[\cancel{\frac{\alpha}{(1+\alpha)}} \cdot \cancel{\frac{p}{p^\ominus}}\right]}{\left[\frac{(1-\alpha)}{\cancel{(1+\alpha)}} \cdot \cancel{\frac{p}{p^\ominus}}\right]} =$$

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

d). $pV = nRT$ & total n @ eqm $= n(1+\alpha)$

$$\Rightarrow p = \frac{n(1+\alpha)RT}{V} \rightarrow \text{sub into } K_p \text{ from c).}$$

$$K_p = \frac{\alpha^2}{(1+\alpha)(1-\alpha)}\frac{p}{p^\ominus} = \frac{\alpha^2}{\cancel{(1+\alpha)}(1-\alpha)}\cdot\frac{n\cancel{(1+\alpha)}RT}{p^\ominus V} =$$

$$= \frac{\alpha^2}{(1-\alpha)}\cdot\frac{nRT}{p^\ominus V}.$$

e). $n = 0.01$; $V = 1\cdot10^{-3}\,m^3$ & $T = 450\,K$, $p^\ominus = 10^5\,Pa$.
from c): $K_p = 0.0495$ & → calculate α:

$$\Rightarrow K_p = \frac{\alpha^2}{(1-\alpha)}\cdot\frac{nRT}{p^\ominus V} \rightarrow \underbrace{\frac{\alpha^2}{1-\alpha} = \frac{K_p\cdot p^\ominus\cdot V}{nRT} = C}$$

$$C = \frac{0.0495\cdot10^5\cdot1\cdot10^{-3}}{0.01\cdot8.314\cdot450} = 0.1323$$, also : $\alpha^2 = C(1-\alpha) =$
$\alpha^2 = C - C\alpha$

$$\Rightarrow \alpha^2 + C\alpha - C = 0 \rightarrow \alpha = \underbrace{\frac{-b\pm\sqrt{b^2-4ac}}{2a}}_{\text{std. solution quadratic eqn.}}$$ "a" = 1, "b" = C, "c" = −1

$$\alpha = \frac{-C\pm\sqrt{C^2+4C}}{2} = 0.303.$$

27) $\Delta_r G^\ominus = -RT\ln K_p$ & $\left(\frac{\partial G/T}{\partial T}\right)_p = -\frac{H}{T^2}$ (Gibbs-Helmholtz)

a).

$$\frac{\partial \ln K_p}{\partial T} = \frac{-1}{R}\frac{\partial}{\partial T}\left(\frac{\Delta_r G^\ominus}{T}\right) = \frac{-1}{R}\cdot\frac{-\Delta_r H^\ominus}{T^2} = \frac{\Delta_r H^\ominus}{RT^2}$$

Gibbs-Helmholtz holds for both products & reactants: $\frac{\partial(\Delta_r G^\ominus/T)}{\partial T} = -\frac{\Delta_r H^\ominus}{T^2}$

so : $\frac{d\ln K_p}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$ (note: $\frac{\partial \ln K_p}{\partial T} = \frac{\Delta_r H^\ominus}{RT^2}$ also ok, as $p = p^\ominus = cst$)

assume indep. of T.

b). $\frac{\partial \ln k_p}{\partial T} = \frac{\Delta_r H^\ominus}{RT^2} \rightarrow \int_{\ln k_p(T_1)}^{\ln k_p(T_2)} d\ln k_p = \frac{\Delta_r H^\ominus}{R} \int_{T_1}^{T_2} \frac{1}{T^2}\, dT$

$$\ln \frac{k_2}{k_1} = \frac{\Delta_r H^\ominus}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2} = -\frac{\Delta_r H^\ominus}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where $k_i = k_p(T_i)$

c). $T_1 = 298k \quad T_2 = 308k \quad k_2 = 2k_1$

$$\Rightarrow \ln \frac{k_2}{k_1} = -\frac{\Delta_r H^\ominus}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \Rightarrow \cancel{\Delta_r H^\theta = -R \ln \frac{k_2}{k_1}}$$

$$\Delta_r H^\theta = -R \cdot \ln \frac{k_2}{k_1} \frac{1}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = -R \ln \frac{k_2}{k_1} \cdot \frac{T_1 T_2}{T_1 - T_2}$$

$$\Delta_r H^\ominus = -8.314 \cdot \ln 2 \cdot \frac{298 \cdot 308}{298 - 308} = 52.9 \cdot 10^3\ J mol^{-1}$$

28 $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$

$\Delta_r G^\ominus = -16.49\ kJ mol^{-1}$ & $\Delta_r H^\ominus = -46.11\ kJ mol^{-1}$

a). $\Delta_r G^\theta = -RT \ln k_p \rightarrow k_p = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{+16.49 \cdot 10^3}{8.314 \cdot 298}\right)$

$$k_p(T = 298k) = 777.21$$

k_p @ $T = 1000k$ & $\Delta_r H^\theta$ is indep. of $T \rightarrow$ Van't Hoff equation (see Exercise 27)

$$\ln \frac{k_2}{k_1} = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$k_1 = 777.21$ @ $T_1 = 298k$
$k_2 = ?$ @ $T_2 = 1000k$

$$\ln \frac{k_2}{k_1} = \frac{+46.11 \cdot 10^3}{8.314} \cdot \left(\frac{1}{1000} - \frac{1}{298}\right) = -13.065 \rightarrow k_2 = 1.646 \cdot 10^{-3}$$

c). $K_2 = 1 \quad T_2 = ? \quad (T_1 = 298K \;\&\; K_1 = 777.21)$

$$\ln\frac{K_2}{K_1} = \frac{-\Delta_r H^\theta}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow \ln\frac{1}{K_1} = \frac{-\Delta_r H^\theta}{R}\left(\frac{1}{T_2} - \frac{1}{\cancel{298}\,T_1}\right)$$

$$\Rightarrow \frac{1}{T_2} = \frac{-R}{\Delta_r H^\theta} \cdot \ln\left(\frac{1}{K_1}\right) + \frac{1}{T_1}$$

$$= \frac{-8.314}{-46.11 \cdot 10^3} \cdot \ln\frac{1}{777.21} + \frac{1}{298} =$$

$$= 0.002155 \quad \Rightarrow T_2 = 463.9\ K$$

d)

	$\frac{1}{2}N_2$	$+\ \frac{3}{2}H_2$	$\rightleftarrows NH_3$	total
N_{init}	0	0	1	1
N_{eqm}	$\frac{1}{2}\alpha$	$\frac{3}{2}\alpha$	$1-\alpha$	$1+\alpha$
X_i	$\frac{\frac{1}{2}\alpha}{1+\alpha}$	$\frac{\frac{3}{2}\alpha}{1+\alpha}$	$\frac{1-\alpha}{1+\alpha}$	1
P_i	$\left(\frac{\frac{1}{2}\alpha}{1+\alpha}\right)p$	$\left(\frac{\frac{3}{2}\alpha}{1+\alpha}\right)p$	$\left(\frac{1-\alpha}{1+\alpha}\right)p$	p

$K_p = 1$

$T = 463.9\,K$

$p = 1\,atm$
$= p^\theta!$

$$K_p = \frac{(P_{NH_3}/p^\theta)}{\left(\frac{P_{N_2}}{p^\theta}\right)^{1/2}\left(\frac{P_{H_2}}{p^\theta}\right)^{3/2}} =$$

$$= \frac{\left[\left(\frac{1-\alpha}{1+\alpha}\right)\frac{p}{p^\theta}\right]}{\left[\left(\frac{\frac{1}{2}\alpha}{1+\alpha}\right)\frac{p}{p^\theta}\right]^{1/2}\left[\left(\frac{\frac{3}{2}\alpha}{1+\alpha}\right)\frac{p}{p^\theta}\right]^{3/2}} = \longrightarrow$$

note
$p = p^\theta$: $\frac{p}{p^\theta} = 1$

$$K_p = \left(\frac{1-\alpha}{1+\alpha}\right) \cdot \left(\frac{\frac{1}{2}\alpha}{1+\alpha}\right)^{-1/2} \cdot \left(\frac{\frac{3}{2}\alpha}{1+\alpha}\right)^{-3/2} =$$

$$= \frac{(1-\alpha)}{(1+\alpha)} \cdot \left(\frac{1+\alpha}{\frac{1}{2}\alpha}\right)^{1/2} \left(\frac{1+\alpha}{\frac{3}{2}\alpha}\right)^{3/2} =$$

$$= \frac{(1-\alpha)}{(1+\alpha)} \cdot 2^{1/2} \cdot \left(\frac{1+\alpha}{\alpha}\right)^{1/2} \cdot \frac{2^{3/2}}{3^{3/2}} \cdot \left(\frac{1+\alpha}{\alpha}\right)^{3/2} =$$

$$= \frac{(1-\alpha)}{(1+\alpha)} \frac{2^{1/2} \cdot 2^{3/2}}{3 \cdot 3^{1/2}} \left(\frac{1+\alpha}{\alpha}\right)^{2} = \frac{2^2}{3\sqrt{3}} \cdot \frac{(1-\alpha)}{\cancel{(1+\alpha)}} \cdot \frac{(1+\alpha)^{\cancel{2}}}{\alpha^2} =$$

$$\boxed{K_p = \frac{4}{3\sqrt{3}} \cdot \frac{(1-\alpha^2)}{\alpha^2} = 1}$$

$\downarrow$

$$4 - 4\alpha^2 = 3\sqrt{3} \cdot \alpha^2 \rightarrow 4 = 3\sqrt{3}\alpha^2 + 4\alpha^2 = \alpha^2(3\sqrt{3}+4)$$

$$\alpha^2 = \frac{4}{(3\sqrt{3}+4)} \Rightarrow \alpha = \left(\frac{4}{3\sqrt{3}+4}\right)^{1/2} = 0.6595$$

$N_2 \rightarrow \alpha/2 = 0.33$

$H_2 \rightarrow 3\alpha/2 = 0.989$

$NH_3 \rightarrow 1-\alpha = 0.34$.

(29) $Al(s) | Al^{3+}(aq) || Sn^{2+}_{(aq)} | Sn(s)$

$E^{\ominus}_{Sn/Sn^{2+}} = -0.136\ V$

$E^{\ominus}_{Al/Al^{3+}} = -1.61\ V$

a) LHS: $\frac{1}{3}Al^{3+} + e^- \rightarrow \frac{1}{3}Al(s)$

RHS: $\frac{1}{2}Sn^{2+} + e^- \rightarrow \frac{1}{2}Sn(s)$ (both a reductions)

cell: RHS − LHS = $\frac{1}{2}Sn^{2+} - \frac{1}{3}Al^{3+} \rightarrow \frac{1}{2}Sn(s) - \frac{1}{3}Al(s)$

$\Rightarrow \frac{1}{2}Sn^{2+}(aq) + \frac{1}{3}Al(s) \rightarrow \frac{1}{2}Sn(s) + \frac{1}{3}Al^{3+}(aq)$.

$E^{\ominus}_{cell} = -0.136 - (-1.61) = 1.474\ V$.

b). Nernst: $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{\nu F} \ln Q$ $\quad Q = \prod_i a_i^{\nu_i}$

$\nu = 1$ & $Q = \frac{a_{Al^{3+}}^{1/3} \cdot a_{Sn(s)}^{1/2}}{a_{Al(s)}^{1/3}\ a_{Sn^{2+}}^{1/2}}$ $\quad$ a solids = 1

$a_{Al^{3+}} = f \cdot \frac{c_i}{c^{\ominus}}$ $\quad$ (i) $c^{\ominus} = 1$ mol dm^{-3} $\quad f = 1$

(ii) $c_{Al^{3+}} = 1$ mol dm^{-3} or 0.1 mol dm^{-3}

$a_{Sn^{2+}} \longrightarrow$ same: $c_{Sn^{2+}} = 1$ or 0.1

(i): $\ln Q = 0$ as $Q = 1 \rightarrow E_{cell} = E^{\ominus}_{cell}$
$= +1.474\,V$

(ii): $\ln Q = \ln \frac{0.1^{1/3}}{0.1^{1/2}} \rightarrow E_{cell} = E^{\ominus}_{cell} - \frac{RT}{F} \ln \frac{0.1^{1/3}}{0.1^{1/2}}$

$= E^{\ominus}_{cell} - 9.86 \cdot 10^{-3} =$

$= 1.474 - 9.86 \cdot 10^{-3} = 1.464\,V.$

c). conc. 1.0M $\rightarrow$ $E_{cell} = E^{\ominus}_{cell} = +1.474\,V$

$\Delta_r G^{\ominus} = -\nu F E^{\ominus}_{cell} = -1 \cdot F \cdot 1.474 = -142.2$ kJ mol^{-1}

$K_p = \exp[-\Delta_r G^{\ominus}/RT] = \exp\left(\frac{+142.2 \cdot 10^3}{8.314 \cdot 298}\right) = 8.44 \times 10^{24}$

Note that there was a mistake in the question, it should have stated:
'Calculate DrG^std and the equilibrium constant for the cell reaction.'

(so without the 'when all activities are 1').

Note that this question has now been split up over multiple parts, answer is the same

$$Pt \,|\, H_2(g)\,(p = 1\,atm) \,|\, HBr\,(10^{-4} M) \,|\, CuBr(s) \,|\, Cu$$

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$E_{cell} = 0.559\,V$

a) RHS: $CuBr(s) + e^- \rightarrow Cu(s) + Br^-(aq)$ $\left(\boxed{E^\ominus_{Cu/CuBr}}\right)$ → to be calculated.

LHS: $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$ $E^\ominus = 0\,V$

RHS-LHS* ~~both half reactions~~

→ cell reaction: $CuBr(s) + \frac{1}{2} H_2(g) \rightarrow Cu(s) + H^+(aq) + Br^-(aq)$

* as both half reactions written as reductions!

Nernst: $E_{cell} = E^\ominus_{cell} - \frac{RT}{F} \ln \frac{a_{H^+} a_{Br^-}}{a_{H_2}^{1/2}}$ [here $\nu = 1$, a solids $= 1$].

$a_{H^+} = a_{Br^-} = 10^{-4}$ (assuming activity coeff $= 1$.)

$a_{H_2} = 1$ $(p = p^\ominus)$.

$$E^\ominus_{cell} = E + \frac{RT}{F} \ln \frac{10^{-4} \cdot 10^{-4}}{1} = 0.559 + \frac{8.314 \cdot 298}{96490} \cdot \ln 10^{-8} =$$

$$= 0.086\,V$$

$$E^\ominus_{cell} = E^\ominus_{RHS} - E^\ominus_{LHS} = E^\ominus_{Cu/CuBr} - 0 = E^\ominus_{Cu/CuBr}$$

↑ std. hydrogen electrode.

$$\Rightarrow E^\ominus_{Cu/CuBr} = 0.086\,V$$

b). we need the cell: $Cu(s) \,|\, Cu^+(aq) \,||\, Br^-(aq) \,|\, CuBr(s) \,|\, Cu(s)$

all as reductions {

RHS: $CuBr(s) + e^- \rightarrow Cu(s) + Br^-(aq)$ $E^\ominus_{RHS} = 0.086\,V$ (from a))

LHS: $Cu^+(aq) + e^- \rightarrow Cu(s)$ $E^\ominus_{LHS} = 0.522\,V$

overall cell: $CuBr(s) \longrightarrow Cu^+(aq) + Br^-(aq)$ $E^\ominus_{cell} = E^\ominus_{RHS} - E^\ominus_{LHS}$

$E^\ominus_{cell} = -0.436\,V$

c) $\Delta_r G^\ominus = -\nu F E^\ominus_{cell} = -1 \cdot 96490 \cdot -0.436 = +42074\,J\,mol^{-1}$

$$K_p = \underbrace{a_{Cu^+} a_{Br^-}}_{\text{solubility product of CuBr}} = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left(-\frac{42074}{8.314 \cdot 298}\right)$$

$$K = 4.22 \cdot 10^{-8}$$

(31) $Pt \mid H_2(g) \mid (p = 1\,atm) \mid HCl\,(a=1) \mid AgCl(s) \mid Ag$

$$E^{\ominus}_{cell} = 0.2366 - 4.856 \cdot 10^{-4}(T-273) - 3.421 \cdot 10^{-6}(T-273)^2$$

RHS: $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$

LHS: $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$

} all as reductions

- Overall cell reaction: $AgCl(s) + \frac{1}{2}H_2(g) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq)$

- ~~for~~ $\Delta_r G^{\ominus} = -\nu F E^{\ominus}_{cell}$ @ $T = 298\,K$.

$$E^{\ominus}_{cell}(T=298) = 0.2366 - 4.856 \cdot 10^{-4}(298-273) - 3.421 \cdot 10^{-6}(298-273)^2$$
$$= 0.2223\,V$$

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus}_{cell} = -1 \cdot 96490 \cdot 0.2223 = -21.45\,kJ\,mol^{-1}$$

- $\Delta_r S^{\ominus} = \nu F \left(\frac{\partial E^{\ominus}_{cell}}{\partial T}\right)$ [from $S = -\left(\frac{\partial G}{\partial T}\right)_p$ ...].

$$\frac{\partial E^{\ominus}_{cell}}{\partial T} = -4.856 \cdot 10^{-4} - 2 \times 3.421 \cdot 10^{-6}(T-273)$$

$$\Rightarrow \Delta_r S^{\ominus} = 96490 \cdot (-4.856 \cdot 10^{-4} - 2 \times 3.421 \cdot 10^{-6}(298-273)) =$$
$$= -63.36\,J\,K^{-1}\,mol^{-1}$$

- $\Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\Delta_r S^{\ominus}$ @ cst. temp.

$$= -21.45 \cdot 10^3 + 298 \cdot -63.36 =$$

$$= -40.33\,kJ\,mol^{-1}$$