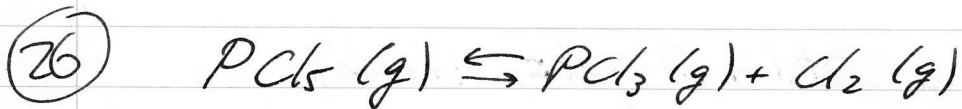


Answers - problem set 6



$$\Delta_r G^\ominus = 83680 - 14.52 T \ln T - 72.26 T$$

$$= a - b T \ln T - c T$$

a) $\rightarrow \Delta_r G^\ominus(T=450\text{K}) = 83680 - 14.52 \cdot 450 \ln 450 - 72.26 \cdot 450$

$$= 11.25 \text{ kJ mol}^{-1}$$

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

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

$$= b \ln T + b + c = 14.52 \ln 450 + 14.52 + 72.26$$

$$= 175.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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	$\left[\frac{(1-\alpha)}{(1+\alpha)}\right] p$	$\left[\frac{\alpha}{(1+\alpha)}\right] p$	$\left[\frac{\alpha}{(1+\alpha)}\right] p$	p

c) $K_p = \prod_i a_i^{v_i} = \prod_i \left(\frac{p_i}{p^\ominus}\right)^{v_i}$

$$K_p = \frac{(p_{\text{Cl}_3}/p^\ominus)(p_{\text{Cl}_2}/p^\ominus)}{(p_{\text{PCl}_5}/p^\ominus)} = \frac{\left[\frac{\alpha}{(1+\alpha)} \cdot \frac{p}{p^\ominus}\right] \left[\frac{\alpha}{(1+\alpha)} \cdot \frac{p}{p^\ominus}\right]}{\left[\frac{(1-\alpha)}{(1+\alpha)} \cdot \frac{p}{p^\ominus}\right]} =$$

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

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

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

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

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

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

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

$$C = \frac{0.0495 \cdot 10^5 \cdot 1 \cdot 10^{-3}}{0.01 \cdot 0.314 \cdot 450} = 0.1323, \text{ also: } \alpha^2 = C(1-\alpha) =$$

$$\alpha^2 = C - C\alpha$$

$$\Rightarrow \alpha^2 + C\alpha - C = 0 \rightarrow \alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

"a" = 1
"b" = C
"c" = -1
std. solution quadratic eqn.

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

27) $\Delta_r G^\ominus = -RT \ln k_p$ & $\left(\frac{\partial \ln k_p}{\partial T}\right)_p = -\frac{H}{T^2}$ (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 $p = p^\ominus = \text{const}$)

assume indep. of T.

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

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

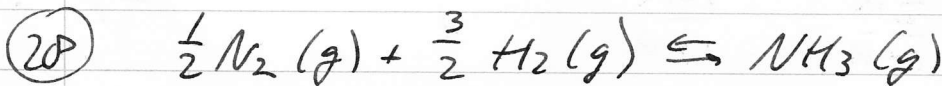
where $k_i = k_p(T_i)$

$$c). T_1 = 298 \text{ K} \quad T_2 = 308 \text{ K} \quad k_2 = 2k_1$$

$$\Rightarrow \ln \frac{k_2}{k_1} = -\frac{\Delta_r H^\ominus}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \Rightarrow \ln 2 = -\frac{\Delta_r H^\ominus}{R} \left[\frac{1}{308} - \frac{1}{298} \right]$$

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

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



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

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

$$k_p(T=298 \text{ K}) = 777.21$$

$k_p @ T=1000 \text{ K}$ & $\Delta_r H^\ominus$ is indep. of T \rightarrow Van't Hoff equation
(see Exercise 27)

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

$$k_1 = 777.21 @ T_1 = 298 \text{ K}$$

$$k_2 = ? @ T_2 = 1000 \text{ K}$$

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

c) ~~$T_2 = ?$~~ $k_2 = 1$ $T_2 = ?$ ($T_1 = 298 \text{ K}$ & $k_1 = 777.21$)

$$\ln \frac{k_2}{k_1} = \frac{-\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \rightarrow \ln \frac{1}{777.21} = \frac{-\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{298} \right)$$

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

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

$$= 0.002155 \Rightarrow T_2 = 463.9 \text{ K}$$

d)

	$\frac{1}{2} \text{N}_2$	$\frac{3}{2} \text{H}_2$	\rightleftharpoons	NH_3	total
init	0	0		1	1
negun	$\frac{1}{2}\alpha$	$\frac{3}{2}\alpha$		$1-\alpha$	$1+\alpha$
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

$$k_p = 1$$

$$T = 463.9 \text{ K}$$

$$p = 1 \text{ atm} = p^\ominus!$$

$$k_p = \frac{(P_{\text{NH}_3}/p^\ominus)}{(P_{\text{N}_2}/p^\ominus)^{1/2} (P_{\text{H}_2}/p^\ominus)^{3/2}} = \frac{\left[\left(\frac{1-\alpha}{1+\alpha} \right) \frac{p}{p^\ominus} \right]}{\left[\left(\frac{\frac{1}{2}\alpha}{1+\alpha} \right) \frac{p}{p^\ominus} \right]^{1/2} \left[\left(\frac{\frac{3}{2}\alpha}{1+\alpha} \right) \frac{p}{p^\ominus} \right]^{3/2}} =$$

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

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

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

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

↓

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

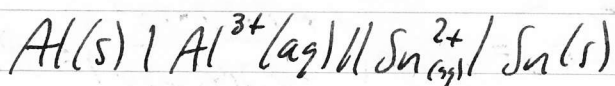
$$\alpha^2 = \frac{4}{3\sqrt{3} + 4} \Rightarrow \alpha = \left(\frac{4}{3\sqrt{3} + 4} \right)^{1/2} = 0.6595$$

$$N_2 \rightarrow \frac{\alpha}{2} = 0.33$$

$$H_2 \rightarrow \frac{3\alpha}{2} = 0.989$$

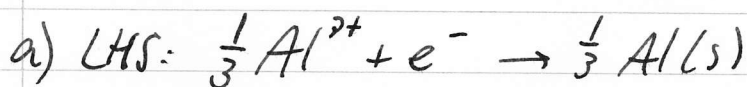
$$NH_3 \rightarrow 1 - \alpha = 0.34$$

(29)

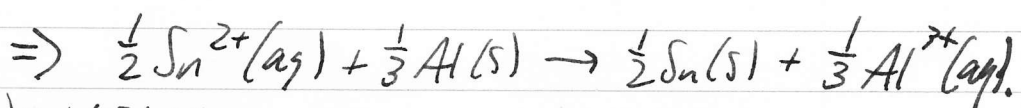
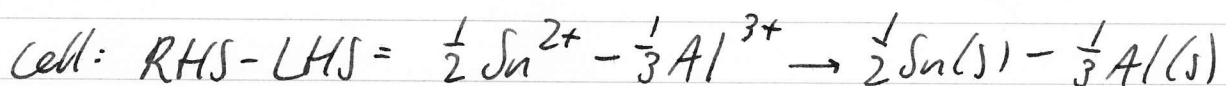


$$E_{Sn^{2+}/Sn}^{\ominus} = -0.136 \text{ V}$$

$$E_{Al^{3+}/Al}^{\ominus} = -1.61 \text{ V}$$



(both a reductions)



$$E_{\text{cell}}^{\ominus} = -0.136 - (-1.61) = 1.474 \text{ V}$$

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

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

$a_{\text{Al}^{3+}} = f \cdot \frac{c_i}{c^{\ominus}}$ (i) $c^{\ominus} = 1 \text{ mol dm}^{-3}$ $f = 1$
 (ii) $c_{\text{Al}^{3+}} = 1 \text{ mol dm}^{-3}$ or 0.1 mol dm^{-3}

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

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

(ii): $\ln Q = \ln \frac{0.1^{1/3}}{0.1^{1/2}} \rightarrow E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{F} \ln \frac{0.1^{1/3}}{0.1^{1/2}}$
 $= E_{\text{cell}}^{\ominus} - 9.06 \cdot 10^{-3} =$
 $= 1.474 - 9.06 \cdot 10^{-3} = 1.464 \text{ V}$

c). $a_{\text{conc.}} = 1.0 \rightarrow E_{\text{cell}} = E_{\text{cell}}^{\ominus} = +1.474 \text{ V}$

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

$K_p = \exp\left[-\frac{\Delta_r G^{\ominus}}{RT}\right] = \exp\left(\frac{+142.2 \cdot 10^3}{8.314 \cdot 298}\right) = 0.44 \cdot 10^{24}$

Note that there was a mistake in the question, it should have stated:

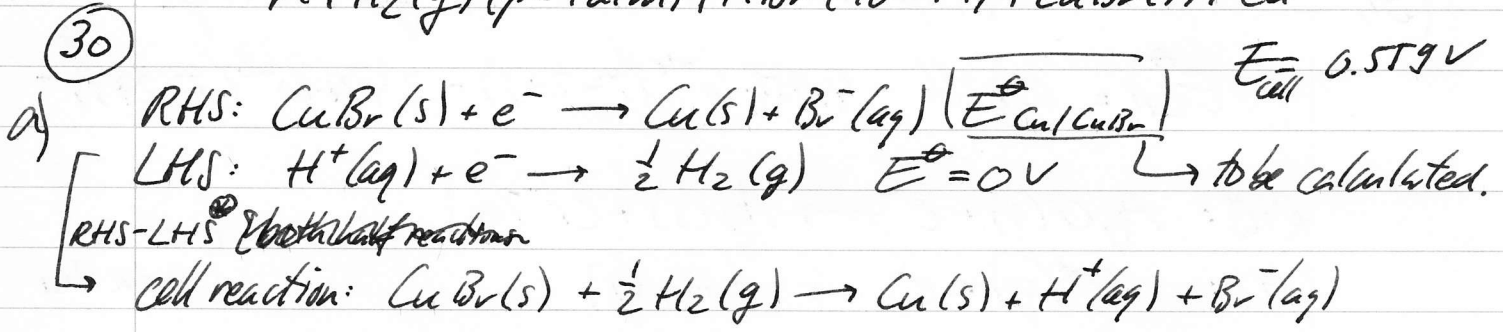
'Calculate $\Delta_r G^{\ominus}$ and the equilibrium constant for the cell reaction.'

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

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



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⊗ as both half reactions written as reductions!

$$\text{Nernst: } E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{F} \ln \frac{a_{\text{H}^+} a_{\text{Br}^-}}{a_{\text{H}_2}} \quad \left[\text{here } \nu=1, \alpha \text{ solids} = 1 \right].$$

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

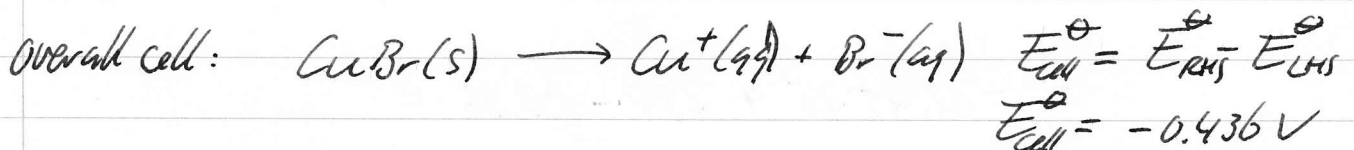
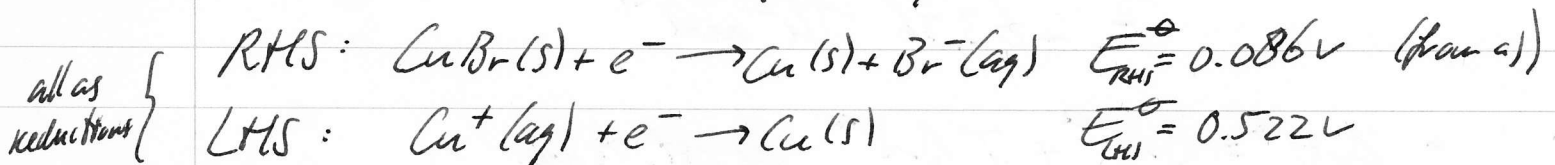
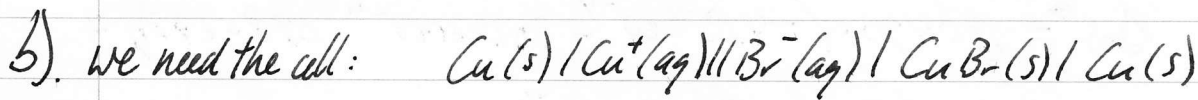
$$a_{\text{H}_2} = 1 \quad (p = p^\ominus).$$

$$E_{\text{cell}} = E + \frac{RT}{F} \ln \frac{10^{-4} \cdot 10^{-4}}{1} = 0.579 + \frac{8.314 \cdot 290}{96490} \cdot \ln 10^{-8} = 0.086\text{V}$$

$$E_{\text{cell}}^\ominus = E_{\text{RHS}}^\ominus - E_{\text{LHS}}^\ominus = E_{\text{Cu/CuBr}}^\ominus - 0 = E_{\text{Cu/CuBr}}^\ominus$$

↑ std. hydrogen electrode.

$$\Rightarrow E_{\text{Cu/CuBr}}^\ominus = 0.086\text{V}$$



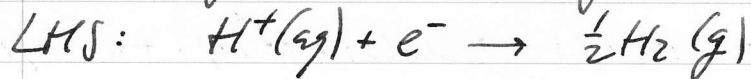
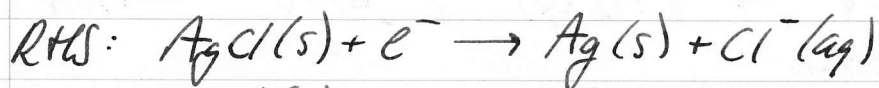
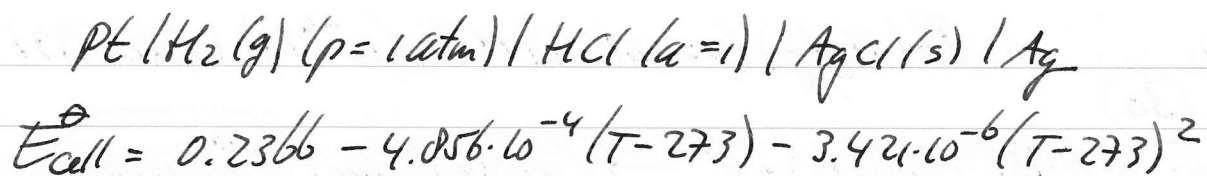
c) $\Delta_r G^\ominus = -\nu F E_{\text{cell}}^\ominus = -1 \cdot 96490 \cdot -0.436 = +42074 \text{ J mol}^{-1}$

$$K_p = a_{\text{Cu}^+} a_{\text{Br}^-} = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left(-\frac{42074}{8.314 \cdot 290}\right)$$

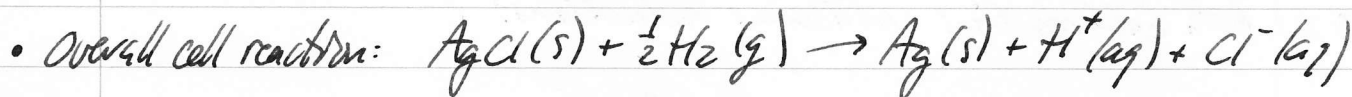
solubility product of CuBr

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

(31)



} all as reductions



• $\Delta_r G^{\ominus} = -\nu F E_{\text{cell}}^{\ominus}$ @ $T = 298 \text{ K}$.

$$E_{\text{cell}}^{\ominus} (T=298) = 0.2366 - 4.056 \cdot 10^{-4} (298-273) - 3.421 \cdot 10^{-6} (298-273)^2$$
$$= 0.2223 \text{ V}$$

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

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

$$\frac{\partial E_{\text{cell}}^{\ominus}}{\partial T} = -4.056 \cdot 10^{-4} - 2 \times 3.421 \cdot 10^{-6} (T-273)$$

$$\Rightarrow \Delta_r S^{\ominus} = 96490 \cdot (-4.056 \cdot 10^{-4} - 2 \times 3.421 \cdot 10^{-6} (298-273)) =$$
$$= -63.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

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