Chem 12 Hw set 8 - non-graded part

A. ch 11, 34 a $I_2 + NaCl(aq)$?

$I_2 + 2Cl^- \longrightarrow 2I^- + Cl_2$ favorable ?

I_2 red $+0.54$ V
Cl^- ox -1.36 V

so $\mathcal{E}^\circ$ would be -0.82 V

so no rxn would occur

(& ΔG° would thus be positive)

b Cl_2 gas $+ NaI(aq)$?

that's just the reverse of the one above -
so $\mathcal{E}^\circ = +0.82$ V

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$
$$= -(2)(96{,}485\ \tfrac{C}{mol})(0.82\ \tfrac{J}{C})$$
$$= -158\ kJ/mol$$
$$K = e^{-\Delta G^\circ/RT}$$
$$= e^{-(-158{,}000\ J/mol)/(8.314\ \frac{J}{mol\,K})(298\,K)}$$
$$= \cancel{5.46 \times 10^{27}}$$
$$5.5 \times 10^{27}$$

yes, I've carried along one more sig fig than I should have - I hate cumulative rounding errors !

38. $2H_2 + O_2 \rightarrow 2H_2O$

$K = 1.28 \times 10^{83}$!

a. $\Delta G^\circ = -RT\ln K$ $T = 298\,K$

$= -474$ kJ/mol

$$\mathcal{E}^\circ = -\frac{\Delta G^\circ}{nF}$$
$$= -\frac{(-474000\ J/mol)}{(4\ e^-\text{'s transferred})(96{,}485\ J/V\,mol)}$$

$1\,C = 1\,J/V$

$= 1.23$ V (as expected)

38 (cont'd) b. $2H_2 + O_2 \rightarrow 2H_2O(l)$

ΔH° - exothermic or endothermic?

The crash of the Hindenburg generated a bit of heat, eh? (Do a Google search on "Hindenburg" if you're not familiar with the famous video.) ΔH° is negative.

3 things → 2 generally has a negative ΔS°

In this case we also have gases → liquid, so ΔS° should be very negative.

c. $\Delta G^\circ = W_{max}$ for the fuel cell rxn.

$$\underset{\text{neg}}{\Delta G^\circ} = \underset{\substack{\uparrow \\ \text{neg}}}{\Delta H^\circ} \underbrace{- T\underset{\substack{\uparrow \\ \text{neg}}}{\Delta S^\circ}}_{\substack{\text{This term makes a positive} \\ \text{contribution to } \Delta G^\circ\text{,} \\ \text{the magnitude of which} \\ \text{increases with T}}}$$

So ΔG° & the maximum work that could be produced would decrease as T increases.

39. We did that in class & in lab.

If ΔS° were ≈ 0, ΔG°, and thus E° would not be strongly temperature-dependent.

Hw set 8 − ng.

41. $H{-}C{\equiv}C{-}H + 4\,F_2 \longrightarrow 2\,CF_4 + H_2$ (Is this a real rxn?! Probably not.)

$\Delta S^\circ = -358\ J/K$ (per mol of $HC{\equiv}CH$)

$= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$

$-358\ \frac{J}{K\,mol} = 2\,S^\circ(CF_4) + 131\ \frac{J}{K\,mol} - 201\ \frac{J}{K\,mol} - 4(203\ \frac{J}{K\,m}$

$S^\circ(CF_4) = 262\ \frac{J}{mol\,K}$

45. Hg $\Delta H_{vap} = 58.51\ kJ/mol$

$\Delta S_{vap} = 92,92\ \frac{J}{mol\,K}$

$$T_b = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{58510\ J/mol}{92,92\ J/mol\,K}$$

$T_b = 629,7\ K$ $(= 331.5\ °C)$

46. $\Delta H_{vap} = 38,7\ kJ/mol$ at $T_b = 351\ K$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = 110\ \frac{J}{K\,mol} \times 1\ mol = 110\ J/K$$

↗ this is positive for the "system" − entropy increases upon going from liquid to vapor

Since vaporization is endothermic, heat flows in from surroundings, so $\Delta S_{surr} = \frac{-38700\ J}{351\ K}$

$= -110\ J/K$

$\Delta S_{univ} = 0$ (this is, for all practical purposes, a reversible process)

13. Ch 10, 30. 1 mol of ICE at $-30°C \longrightarrow$ 1 mol of steam at 140°C

$P = 1$ atm.

let's start with ICE at $-30°C$ & work our way up

— $140°C = 413K$

steam ΔT $C_p = 36.4 \ J/mol\,K$

$\Delta S = nC_p \ln \frac{T_2}{T_1} = 3.71 \ J/K$

$q = nC_p\Delta T = 1.456 \ kJ$

$\Delta H = q = 1.456 \ kJ$

$w = -P\Delta V = -nR\Delta T = -0.332 \ kJ$

— $100°C$

phase change $\Delta H_{vap} = 40.7 \ kJ/mol$

$\Delta S = \frac{\Delta H_{vap}}{T} = 109.1 \ J/K$

$q = \Delta H = 40.7 \ kJ$

$w = -P\Delta V \approx -P V_{gas} = -nRT = -3.10 \ kJ$

(ignoring vol of liquid)

— $100°C = 373K$

liquid water ΔT $C_p = 75.3 \ J/mol\,K$

$\Delta S = nC_p \ln \frac{T_2}{T_1} = 23.50 \ J/K$

$q = nC_p\Delta T = 7.53 \ kJ$

$\Delta H = q = 7.53 \ kJ$

$w = 0$ again

$(\Delta V \approx 0)$

— $0°C$

phase change $\Delta H_{melt} = 6.01 \ kJ/mol$

$\Delta S = \frac{\Delta H_{melt}}{T} = 22.01 \ J/K$

$q = \Delta H = 6.01 \ kJ$

$w = 0$

— $0°C = 273K$

ICE ΔT $C_p = 37.5 \ J/mol\,K$

$\Delta S = nC_p \ln \frac{T_2}{T_1} = 4.365 \ J/K$

$q = nC_p\Delta T = 1.13 \ kJ$

$\Delta H = q = 1.13 \ kJ$

$w = 0$ (no vol. change)

— $-30°C = 243K$

$\boxed{1 \text{ mol } H_2O}$

now, adding these up, we have:

$\Delta S = 163 \ J/K$

$\Delta H = 56.8 \ kJ$

$q = 56.8 \ kJ$

$w = -3.43 \ kJ$

↑ negative ⇒ system did work on surroundings due to the formation & expansion of the steam

50. b. $6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2$
glucose

	$6\,CO_2(g)$ +	$6\,H_2O(l)$ ⟶	$C_6H_{12}O_6(s)$	+ $6\,O_2$
$n \times \Delta G_f^\circ$:	6×-394	6×-237	-911	6×0 kJ/mol
$n \times \Delta H_f^\circ$:	$6 \times -393{,}5$	6×-286	-1275	6×0 kJ/mol
$n \times S^\circ$:	6×214	6×70	212	6×205 J/K

$\Delta G^\circ = +2875$ kJ/mol   from ΔG_f° s
$\Delta H^\circ = +2802$ kJ/mol   from ΔH_f° s
$\Delta S^\circ = -262$ J/K   from S° s

we can also calculate ΔG° from ΔH° + ΔS° —

$$\Delta G^\circ = 2802\ \text{kJ/mol} - (298\,\text{K})(-0{,}262\ \text{kJ/K})$$
$$= 2880\ \text{kJ/mol}\ ✓$$

that's easier.

c. $P_4O_{10}(s) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(s)$

as above . . .

$\Delta H^\circ = -416$ kJ/mol
$\Delta S^\circ = -209$ J/K
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -354$ kJ/mol

57. see text answer

59. " " "

75. $HgbO_2 \rightleftharpoons \cancel{Hgb} + O_2$ $\Delta G^\circ = +70$ kJ/mol
$\cancel{Hgb} + CO \rightleftharpoons HgbCO$ $\Delta G^\circ = -80$ kJ/mol
$HgbO_2 + CO \rightleftharpoons HgbCO + O_2$ $\Delta G^\circ = -10$ kJ/mol $\Rightarrow K = e^{-\Delta G^\circ/RT}$
$K = 57$

91. $K_a = 7{,}2 \times 10^{-4}$ at 298 K $\Rightarrow$
$\Delta G^\circ = +18$ kJ/mol

$$\Delta G = \Delta G^\circ + RT \ln \frac{[H^+][F^-]}{[HF]}$$

b. I get $\Delta G = +0{,}081$ so this is very close to equilib.
d. That one is zero... $\Delta G = 0 \Rightarrow$ this is <u>at</u> equilib.