Day 1 : Chp 17 (17.1-17.4) p. 823 (#25, 29-39 odd)

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25) A, B, C : From our own experiences, we know that salt water, colored water & rust form w/o any outside intervention. A bedroom, however spontaneously gets cluttered. Takes outside source to clean it.

29a) All the possible arrangements:

2 KJ	—	—	X	—	X	XX
1 KJ	—	X	—	XX	X	—
0 KJ	XX	X	X	—	—	—
Total E	0 KJ	1 KJ	2 KJ	2 KJ	3 KJ	4 KJ

Most likely is 2 KJ.

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31) a) H_2 at 100°C & 5 atm; ↑ temp & ↓ press. = ↑ vol. and ∴ ↑ pos. entropy.

b) N_2 at STP has greater volume.

c) $H_2O(l)$ is more disordered than $H_2O(s)$.

Boiling requires heat → endo. All endo ↓ S_{surr}

33) a) − ΔS (more entropy as a gas, so less in surrounding)

b) + ΔS (less entropy as a solid, so more in surrounding) (Exo)

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35) $\Delta G = \Delta H - T\Delta S$; When ΔG is (−), it is spon.

a) $\Delta G = \Delta H - T\Delta S = 25\times10^3\,J - (300.\,K)(5.0\,J/K) = \boxed{24{,}000\,J \text{ not spon.}}$

b) $\Delta G = 25{,}000\,J - (300.\,K)(100.\,J/K) = \boxed{-5{,}000\,J \text{ spon.}}$

c) ΔH is (−), ΔS is (+), so ΔG is (−) @ all temps.

d) $\Delta G = (-1.0\times10^4\,J) - (200.\,K)(-40.\,J/K) = \boxed{-2000\,J \text{ spon.}}$

37) $\Delta G = \emptyset$ b/c @ equilibrium when b.p.

$$\Delta H = T\Delta S$$

$$\frac{(27500\ J/mol)}{(35+273\ K)} = \Delta S = \boxed{89.3\ J/K\cdot mol}$$

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39) a) $NH_3(s) \rightarrow NH_3(l)$; $\Delta G = \Delta H - T\Delta S =$ ~~5650 J/mol~~

~~200K~~

$$\Delta G = 5650\ \frac{J}{mol} - 200K\left(28.9\ \frac{J}{K\cdot mol}\right)$$

$\boxed{\Delta G = -130\ \frac{J}{mol}}$ $\boxed{\text{Yes, } NH_3 \text{ will melt, since } \Delta G < 0 \text{ @ this temp.}}$

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(39) b) At the melting point, $\Delta G = 0$,

$$\text{so } T = \frac{\Delta H}{\Delta S} = \frac{5650\ \frac{J}{mol}}{28.9\ \frac{J}{K\cdot mol}}$$

$$\boxed{T = 196K}$$

Day 2: Chp. 17 (17.5-17.6) p. 824 (# 41-53 odd, 57, 59)

41) a) Decrease in disorder; ΔS° (−)

b) " " "

c) " " "

d) Increase in disorder; ΔS° (+)

43) a) $C_{graphite}(s)$; Diamond is more ordered than graphite.

b) $C_2H_5OH(g)$; Gas is more disordered than liquid.

c) $CO_2(g)$; gas is more disordered than solid.

45) a) $2H_2S(g) + SO_2(g) \rightarrow 3\,S_{rhombic}(s) + 2H_2O(g)$

Since there are more molecules of reactant gas as compared to product ($\Delta n = 2-3 < 0$), ΔS° will be (−).

$$\Delta S^\circ = \sum n_p S^\circ_{prod.} - \sum n_r S^\circ_{react.}$$

From A21 Appendix in back

$$\Delta S^\circ = \left[3\,\text{mol}_{S_{rhom}}\left(32\,\frac{J}{K\cdot mol}\right) + 2\,\text{mol}_{H_2O(g)}\left(189\,\frac{J}{K\cdot mol}\right)\right] - \left[2\,\text{mol}\,H_2S\left(206\,\frac{J}{K\cdot mol}\right) + 1\,\text{mol}\,SO_2\left(248\,\frac{J}{K\cdot mol}\right)\right]$$

$$\Delta S^\circ = 474\,\frac{J}{K} - 660\,\frac{J}{K} = \boxed{-186\,J/K}$$

b) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

Since Δn of gases is (+) ($\Delta n = 3-2$), then ΔS° will be (+).

$$\Delta S = \left[2\,\text{mol}\left(248\,\frac{J}{K\cdot mol}\right) + 1\,\text{mol}\left(205\,\frac{J}{K\cdot mol}\right)\right] - \left[2\,\text{mol}\left(257\,\frac{J}{K\cdot mol}\right)\right] =$$

$$\boxed{\Delta S = 187\,J/K}$$

45) c) $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

Δn gases = 0 $(\Delta n = 3-3)$, can't predict ΔS.

$$\Delta S = \left[2\left(27 \frac{J}{K \cdot mol}\right) + 3(189)\right] - \left[90 + 3(131)\right]$$

$$\boxed{\Delta S = 138\ J/K}$$

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47) $C_2H_2 + 4F_2 \rightarrow 2CF_4 + H_2$

$$\Delta S^\circ = 2S^\circ_{CF_4} + S^\circ_{H_2} - \left[S^\circ_{C_2H_2} + 4S^\circ_{F_2}\right]$$

$$-358\ J/K = 2(S^\circ_{CF_4}) + 131 \frac{J}{K} - \left[201 \frac{J}{K} + 4\left(203\ J/K\right)\right]$$

$$\boxed{S^\circ_{CF_4} = 262 \frac{J}{K \cdot mol}}$$

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49) $S_{rhombic} \rightarrow S_{monoclinic}$; This phase transition

a) is spontaneous $(\Delta G < 0)$ at temps above 95°C.

$\Delta G = \Delta H - T\Delta S$.

For ΔG to be (−) only above a certain temp, then ΔH is (+) and ΔS is (+).

b) Since ΔS is (+), then $S_{rhombic}$ is the more ordered crystal structure.

51 a) When a bond is formed, energy is released, so ΔH is (−). Since there are more reactant molecules of gas than product molecules of gas ($\Delta n < 0$), then ΔS will be (−).

51 b) $\Delta G = \Delta H - T\Delta S$; For the rxn to be spon. ($\Delta G < 0$), the favorable enthalpy term must dominate. The rxn will be spon. @ ↓ temps where ΔH dominates.

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53) See Appendix 4

a) $\Delta H^\circ = \sum n_p \Delta H^\circ_{f\,prod} - \sum n_r \Delta H^\circ_{f\,react.}$

$= 2(-242) + 1(-393.5) - [1(-75)]$

$\boxed{\Delta H^\circ = -803 \text{ kJ}}$

$\Delta S^\circ = \sum n_p S^\circ_{prod.} - \sum n_r S^\circ_{react.}$

$= 2(189) + 214 - [186 + 2(205)]$

$\boxed{\Delta S^\circ = -4 \text{ J/K}}$

Two ways to get ΔG°

1) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Be careful of units!)

$\Delta G^\circ = (-803 \times 10^3 \text{ J}) - (298 \text{ K})(-4 \text{ J/K})$

$\boxed{\Delta G^\circ = -8.02 \times 10^5 \text{ J}}$

Or we could use ΔG°_f values: $\Delta G^\circ = \sum n_p \Delta G^\circ_{f\,prod.} - \sum n_r \Delta G^\circ_{f\,react}$

53) b) $\Delta H^\circ = -1275 - [6(-286) + 6(-393.5)] = 2802\ kJ$

$\Delta S^\circ = 6(205) + 212 - [6(214) + 6(70.)] = -262\ J/K$

$\Delta G^\circ = 2802\ kJ - (298\ K)(-0.262\ kJ/K) = \boxed{2880.\ kJ}$

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c) $\Delta H^\circ = 4(-1279) - [1(-2984) + 6(-286)] = -416\ kJ$

$\Delta S^\circ = 4(110.) - [229 - 6(70.)] = -209\ J/K$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -416\ kJ - (298\ K)(-0.209\ kJ/K)$

$\boxed{\Delta G^\circ = -354\ kJ}$

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d) $\Delta H^\circ = -314 - [-92 - 46] = -176\ kJ$

$\Delta S^\circ = 96 - [187 + 193] = -284\ J/K$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -176\ kJ - (298\ K)(-0.284\ kJ/K)$

$\boxed{\Delta G^\circ = -91\ kJ}$

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57) $CH_4 \rightarrow 2H_2 + C$

$\cancel{(2H_2(g) + C(s) \rightarrow CH_4(g))}$ $\Delta G^\circ = (-51\ kJ)$ (-1)

$2H_2(g) + O_2(g) \rightarrow 2H_2O$ $\Delta G^\circ = -474\ kJ$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^\circ = -394\ kJ$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$(51\ kJ) + (-474\ kJ) + (-394\ kJ) = \boxed{-817\ kJ}$

59) $\Delta G^\circ = \sum n_p \Delta G^\circ_f \text{ prod.} - \sum n_r \Delta G^\circ_f \text{ react.}$

$-374\text{ kJ} = -1105\text{ kJ} - \Delta G_f^\circ\ SF_4$

$$\boxed{\Delta G_f^\circ\ SF_4 = -731\ \text{kJ/mol}}$$

Day 3: chp. 17 (17.-7 → end) p. 826 (65, 67, 69, 71, 77)

65) $\Delta G = \Delta G^\circ + RT \ln Q$

For this reaction, $\Delta G = \Delta G^\circ + RT \ln \frac{P_{NO_2} \times P_{O_2}}{P_{NO} \times P_{O_3}}$

$\Delta G^\circ = 1(52\ kJ/mol) + 1(0) - [1(87) + 1(163)] = \underline{-198\ kJ}$

$\Delta G = -198\ kJ + \frac{8.3145\ J/K\cdot mol}{1000\ J/kJ}(298\ K) \ln \frac{(1.0 \times 10^{-7})(1.0 \times 10^{-3})}{(1.0 \times 10^{-6})(2.0 \times 10^{-6})}$

$\Delta G = -198\ kJ + 9.69\ kJ = \boxed{-188\ kJ}$

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67) $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln \frac{P_{N_2O_4}}{(P_{NO_2})^2}$

$\Delta G^\circ = 1(98) - 2(52) = -6\ kJ$

a) These are standard conditions, so $\boxed{\Delta G = \Delta G^\circ}$ since $Q = 1$ and $\ln 1 = 0$. Since ΔG° is (−), the forward rxn is spon. The rxn shifts → to reach equil.

b) $\Delta G = (-6 \times 10^3\ J) + (8.3145\ \frac{J}{K\cdot mol})(298\ K) \ln \frac{0.50}{(0.21)^2}$

$\Delta G = (-6 \times 10^3\ J) + (6.0 \times 10^3\ J) \boxed{= 0}$

Since $\Delta G = 0$, this rxn is @ equil. (No shift.)

c) $\Delta G = (-6 \times 10^3\ J) + (8.3145\ \frac{J}{K\cdot mol})(298\ K) \ln \frac{1.6}{(0.29)^2}$

$\boxed{\Delta G = 1 \times 10^3\ J}$

Since ΔG is (+), the reverse rxn is spon., so the rxn shifts ← to reach equil.

69) $NO_{(g)} + O_{3(g)} \rightleftharpoons NO_{2(g)} + O_{2(g)}$

$$\Delta G^\circ = \sum n_p \Delta G^\circ_{f\,prod.} - \sum n_r \Delta G^\circ_{f\,react}$$

$$\Delta G^\circ = 1(52) - [1(87) + 1(163)] = -198\ kJ$$

$$\Delta G^\circ = -RT \ln K, \quad K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\left(\frac{-(-1.98 \times 10^5 J)}{(8.3145)(298K)}\right)}$$

$$= e^{79.912} = \boxed{K = 5.07 \times 10^{34}}$$

Note: when doing exponents, round @ the end of the calc.

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71) $\Delta G^\circ = \Delta H - T\Delta S$

$$\Delta G^\circ = (-58.03\ kJ/mol) - (298K)(-0.17666\ kJ/K \cdot mol)$$

$$\Delta G^\circ = -5.4\ kJ/mol = -5400\ J/mol$$

0.0789

↑ Not sure how they got this!

$$\Delta G^\circ = -RT \ln K$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\left(\frac{-(-5400\ J/mol)}{(8.3145)(298K)}\right)} = e^{2.179} = \boxed{8.84 = K}$$

~~@400°C~~ ~~0.0789~~ ~~$\Delta G = -54.4\ kJ/mol = -51{,}400\ J/mol$~~

~~0.0789 ← Not sure how they got this!~~

~~73)~~

~~$\frac{1}{2}H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O_2$~~

~~140 kJ~~ ~~$-\frac{1}{2}(2H_2 + O_2 \rightleftharpoons 2H_2O)$~~

~~$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$~~

~~$\Delta G^\circ = -RT \ln K = -73076.6\ J/m$~~

~~$\Delta G^\circ = \ldots = (5.1461 \times 7) - \frac{1}{2}$~~

~~Flip & multiply 2nd rxn by $\frac{1}{2}$~~

77) $K = \dfrac{P_{NF_3}^2}{P_{N_2} \times P_{F_2}^3} = \dfrac{(0.48)^2}{(0.021)(0.063)^3} = 4.4 \times 10^4$

$\Delta G^\circ_{800} = -RT \ln K = -8.3145 \frac{J}{K \cdot mol} (800. K) \ln (4.4 \times 10^4)$

$= -7.1 \times 10^4 \, J/mol = \boxed{-71 \, kJ/mol}$