Homework #5

1. a. i.

$$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4NO_{3(s)} \longrightarrow 2NH_{3(aq)} + 10H_2O_{(l)} + Ba(NO_3)_{2(s)}$$

	$Ba(OH)_2 \cdot 8H_2O_{(s)}$	$2NH_4NO_{3(s)}$	$2NH_{3(aq)}$	$10H_2O_{(l)}$	$Ba(NO_3)_{2(s)}$
ΔH_f kJ/mol	-3342	-365.6	-80.29	-285.83	-992.07
ΔS_{298} J/mol·K	427	157.1	111	69.91	214

$\Delta H_{rxn} = -992.07 + 10(-285.83) + 2(-80.29) - 2(-365.6) - (-3342)$
$= 62.25$ kJ/mol $\boxed{\text{Endothermic}}$

ii. $T\Delta S$ must be greater than ΔH so $\Delta H - T\Delta S$ is negative.

iii.
$\Delta S_{rxn} = 214 + 10(69.91) + 2(111) - 2(157.1) - 427 = 405.9$ J/mol·K
$= 0.4059$ kJ/mol·K

$\Delta G = \Delta H_{rxn} - T\Delta S_{rxn} = 62.25 - 298(0.4059) = 62.25 - 120.96$
$= -58.71$ kJ/mol

spontaneous rxn b/c $T\Delta S > \Delta H$

b. i. $C_{12}H_{22}O_{11} + \cancel{12O_2} \longrightarrow \cancel{12CO_2} + 11H_2O$ $\quad \Delta H_{comb} = -5640.9$ kJ/mol

$\cancel{12CO_2} \longrightarrow \cancel{12O_2} + 12C(graphite)$ $\quad \Delta H = -12\Delta H_f = 4722$ kJ/mol

$C_{12}H_{22}O_{11} \longrightarrow 12C(graphite) + 11H_2O$

$\Delta H_{rxn} = \Delta H_{comb} + (-12\Delta H_f(CO_2))$
$= -5640.9 + 4722$ kJ/mol $= -918.9$ kJ/mol
$\boxed{\text{Endothermic}}$

ii. $70g \times \frac{1 \text{ mol}}{342.2992g} = 0.20$ mol

$q = \Delta H \cdot n = (-918.9 \text{ kJ/mol})(0.20 \text{ mol}) = -187.91$ kJ
Heat evolved = ~188 kJ

iii. density $H_2SO_4 \cdot nH_2O$: 1.84 g/mL $\quad$ mw = 98.07 g/mol
$(70 \cancel{mL})(1.84 g/\cancel{mL})(\frac{1 \text{ mol}}{98.07g}) = 1.31$ mol
$(-40.58 \text{ kJ/mol})(1.31 \text{ mol}) = -53.3$ kJ
Heat evolved = ~53 kJ

iv. 188 + 53 = 241 kJ heat evolved

2. a. $\Delta n_{gas} = (2+1) - 0 = 3$

$\boxed{\Delta H = \Delta U + \Delta n_{gas} RT}$ $\quad \therefore \Delta H > \Delta U$

b. $\Delta n_{gas} = 8 - 8 = 0$ $\quad \Delta H = \Delta U$

or $\Delta H > \Delta U$ b/c volume change from solid to gas... $\Delta H = \Delta U + \Delta(PV)$

3. $P_1, V_1, T_1 \longrightarrow P_2, V_2, T_2$

$V_1 = \frac{nRT_1}{P_1}$ $\quad V_2 = \frac{nRT_2}{P_2}$

$= 11.35 dm^3$ $\quad = 22.70 dm^3$

$2 \text{ bar}, 11.35 dm^3, 273 K \longrightarrow 4 \text{ bar}, 22.70 dm^3, 1092 K$

$\Delta U = n \int_{T_1}^{T_2} \bar{C}_V dT = n \bar{C}_V \Delta T$

$= (1 mol)(12.5 J/mol \cdot K)(1092K - 273K) = 10200 J = 10.2 kJ$

$w = -\int_{V_1}^{V_2} P dV$ $\quad P \neq$ constant

but $P/V = \text{constant} = 0.176 \frac{bar}{dm^3}$

$P = \text{constant} \cdot V = 0.176 \text{ bar/dm}^3 \cdot V$

$= -\int_{V_1}^{V_2} 0.176 V dV$

$= -0.176 \frac{V^2}{2} \Big|_{V_1}^{V_2}$ $\quad V_2 = 22.70 dm^3, \; V_1 = 11.35 dm^3$

$= \frac{-0.176}{2} (22.70^2 - 11.35^2)$

$= -34 \text{ bar} \cdot dm^3 = -3400 J = -3.4 kJ$

$q = \Delta U - w = 10.2 kJ - (-3.4 kJ) = 13.6 kJ$

$\Delta H = \Delta U + nR\Delta T \doteq$ b/c n is constant but T is not

$= 10.2 kJ + (1 mol)(8.314 \frac{J}{K \cdot mol})(1092 - 273 K)(\frac{1 kJ}{1000 J})$

$= 17.0 kJ$

4. $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\bar{C}_V}$ for reversible / adiabatic

$\bar{C}_V = 5R/2 \leftarrow$ diatomic ideal gas (neglecting vibration)

$\frac{R}{\bar{C}_V} = \frac{\cancel{R}}{5/2\cancel{R}} = 2/5$

$T_2 = \left(\frac{V_1}{V_2}\right)^{2/5} \cdot T_1 = \left(\frac{20 dm^3}{5 dm^3}\right)^{2/5} \cdot 298K = 519K$

5. $w_{rev} = -nRT \ln V_2/V_1$ gives minimum work required for compression or maximum work out for expansion

$= -(10 mol)(8.314 J/mol \cdot K)(500K) \ln(40 dm^3/100 dm^3)$

$= 38.090 J$ or $38 kJ$

6. (see Ex 19-11) $CCl_{4(l)} \rightarrow CCl_{4(g)}$

$\Delta H_{vap} = \Delta_f H°[g] - \Delta_f H°[l]$

$= -102.9 - (-135.44)$

$= 32.5 kJ/mol$

7. 19-2 (see Ex 19-1, pg 768)

$P_f = \frac{P_i V_i}{V_f} = \frac{(2.50 dm^3)(3.00 bar)}{(0.500 dm^3)} = 15.0 bar$

$w = -P_{ext}\Delta V = -15.0(0.5 - 2.50) = 30 bar \cdot dm^3 = 3000 J$

[b/c 1 bar·dm³ = 100 J]
(think of R or see pg. 768)

19-7

a) 2.25 L @ 1.33 bar $\longrightarrow$ 1.50 L @ 2.00 bar
where $P_{ext} = 2.00 bar$

$w = -P_{ext}\Delta V = -2.00 bar(1.50 - 2.25 L) = 1.5 bar \cdot L$

$= 150 J$

b) 1.50 L @ 2.00 bar $\rightarrow$ 0.800 L @ 3.75 bar

$P_{ext} = 3.75$ bar

$w = -P_{ext}\Delta V = -3.75\text{ bar}(0.800 - 1.50L) = 2.63\text{ bar}\cdot L$

$= 263\text{ J}$

Total $w = 150 + 263 = \boxed{413\text{ J}}$

c) $w_{rev} = -nRT\ln(V_2/V_1)$ * ideal gas $nRT = PV$ *

choose 1 set ... $(2.25L)(1.33\text{ bar})$

$= 3\text{ L}\cdot\text{bar}$

$= 300\text{ J}$

$= -300\text{ J}\ln(0.8/2.25)$

$= \boxed{-310.2\text{ J}}$

$w_{rev} < w_{isothermal}$ (as expected)

19-44   Eq 19.57

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta C_p(T)\,dT$$

$T_1 = 298K$

$T_2 = 1000K$ $\Delta_r H^\circ(298) = -393.509\text{ kJ/mol}$

Rxn: $C(s) + O_2(g) \longrightarrow CO_2(g)$

$$\Delta C_p(T) = C_p[CO_2](T) - C_p[O_2](T) - C_p[C](T)$$

$$\frac{\Delta C_p(T)}{R} = (2.593 + 7.661\times10^{-3}T - 4.78\times10^{-6}T^2 + 1.16\times10^{-9}T^3)$$
$$- 3.094 - 1.561\times10^{-3}T + 4.65\times10^{-7}T^2$$
$$- (-0.6366) - 7.049\times10^{-3}T + 5.20\times10^{-6}T^2 - 1.38\times10^{-9}T^3$$
$$\overline{0.1356 - 9.49\times10^{-4}T + 8.85\times10^{-7}T^2 - 2.2\times10^{-10}T^3}$$

$$R\int_{298}^{1000} 0.1356 - 9.49\times10^{-4}T + 8.85\times10^{-7}T^2 - 2.2\times10^{-10}T^3\,dT$$

$$R\left[0.1356T - \frac{9.49\times10^{-4}T^2}{2} + \frac{8.85\times10^{-7}T^3}{3} - \frac{2.2\times10^{-10}T^4}{4}\right]\Bigg|_{298}^{1000}$$

$R[-98.9 - (5.64)]$

$= (8.314\text{ J/K}\cdot\text{mol})(-104.54K) = -869.2\text{ J/mol}$

$\Delta_r H(1000K) = -393.509\text{ kJ/mol} - 0.8692\text{ kJ/mol}$

$= -394.38\text{ kJ/mol}$