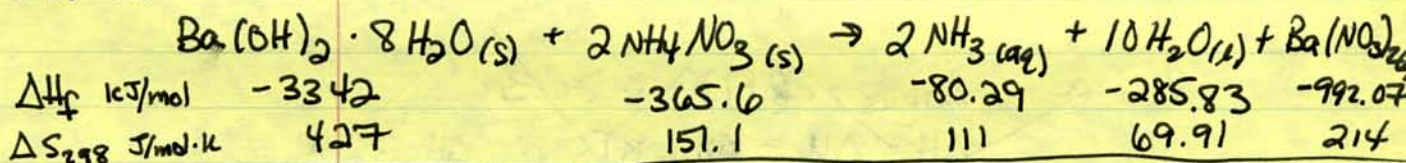


HWK #3

1

1 a (i)



$$\Delta H_{\text{rxn}} = -992.07 + 10(-285.83) + 2(-80.29) - 2(-365.6) - (-3342)$$

$$= 62.25 \text{ kJ/mol}$$

Endothermic

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

(iii)

$$\Delta S_{\text{rxn}} = 214 + 10(69.91) + 2(111) - 2(157.1) - 427 = 405.9 \text{ J/mol}\cdot\text{K}$$

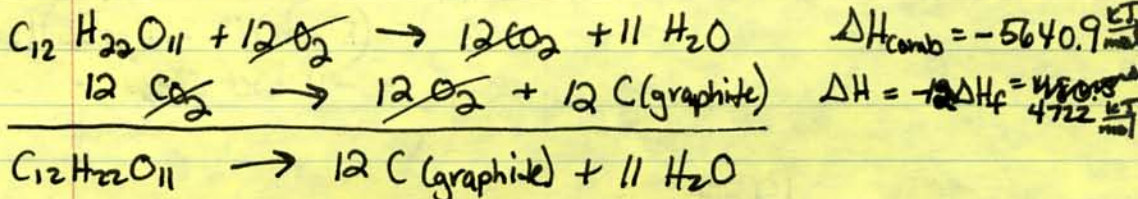
$$= 0.4059 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta G = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = 62.25 - 298(0.4059) = 62.25 - 120.96$$

$$= -58.71 \text{ kJ/mol}$$

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

b (i)



$$\Delta H_{\text{rxn}} = \Delta H_{\text{comb}} + (-12\Delta H_f(\text{CO}_2))$$

$$= -5640.9 + 4722 \text{ kJ/mol} = -918.9 \text{ kJ/mol}$$

Exothermic

(ii) $70 \text{ g} \times \frac{1 \text{ mol}}{342.29 \text{ g}} = 0.20 \text{ mol}$

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

Heat evolved: 188 kJ

(iii) density $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$: 1.84 g/mL

$$(70 \text{ mL})(1.84 \text{ g/mL}) \left(\frac{1 \text{ mol}}{98.07 \text{ g}}\right) = 1.31 \text{ mol}$$

$$(-40.58 \text{ kJ/mol})(1.31 \text{ mol}) = -53.3 \text{ kJ}$$

Heat evolved: ~53 kJ

(iv) $188 + 53 = 241 \text{ kJ}$ heat evolved

(2 below)
3.

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$$

$$V_1 = \frac{nRT_1}{P_1} = 11.35 \text{ dm}^3$$

$$V_2 = \frac{nRT_2}{P_2} = 22.70 \text{ dm}^3$$

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

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

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

$$W = - \int_{V_1}^{V_2} P dV$$

P ≠ constant

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

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

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

$$= -0.176 \left[\frac{V^2}{2} \right]_{V_1}^{V_2} \quad V_2 = 22.70 \text{ dm}^3, V_1 = 11.35 \text{ dm}^3$$

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

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

$$q = \Delta U - W = 10.2 \text{ kJ} - (-3.4 \text{ kJ}) = 13.6 \text{ kJ}$$

$$\Delta H = \Delta U + nR\Delta T =$$

b/c n is constant but

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

$$= 17.0 \text{ kJ}$$

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

$$\Delta H = \Delta U + \Delta n_{\text{gas}} RT$$

$$\therefore \Delta H > \Delta U$$

b $\Delta n_{\text{gas}} = 8 - 8 = 0$

$$\Delta H = \Delta U$$

~~4a)~~

4a) Adiabatic : $\delta q = 0$ $du = \delta w$ $du = n \bar{c}_v dT = \delta w$

$$\delta w = -P dV = -\frac{nRT}{V} dV$$

$$n \bar{c}_v dT = -n \frac{RT}{V} dV$$

see p. 777

$$\int_{T_1}^{T_2} \frac{\bar{c}_v}{T} dT = \int_{V_1}^{V_2} -\frac{R}{V} dV$$

$$\bar{c}_v \ln(T_2/T_1) = -R \ln(V_2/V_1)$$

$$\ln(T_2/T_1)^{\bar{c}_v} = \ln(V_2/V_1)^{-R}$$

$$\left(\frac{T_2}{T_1}\right)^{\bar{c}_v} = \left(\frac{V_2}{V_1}\right)^{-R}$$

or $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\bar{c}_v}$ QED.

~~4b)~~

4b

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\bar{c}_v} \text{ for reversible / adiabatic}$$

$\bar{c}_v = 5R/2$ ← diatomic ideal gas (neglecting vibration)

$$\frac{R}{\bar{c}_v} = \frac{R}{5/2 R} = 2/5$$

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

1c. ~~The heat involved is roughly of the same magnitude~~

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

~~$\Delta H = \Delta U + \Delta n_{\text{gas}} RT \therefore \Delta H > \Delta U$~~

b ~~$\Delta n_{\text{gas}} = 8 - 8 = 0 \therefore \Delta H = \Delta U$~~

5.4.3. M+S problems

19-2 (see Example 19-1 page 768)

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

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

[b/c $1 \text{ bar} \cdot \text{dm}^3 = 100 \text{ J}$
(think of R or see pg 768)]

19-6

minimum amt work = reversible compression

$$W_{\text{rev}} = -nRT \ln(V_2/V_1)$$

$$= (5 \text{ mol})(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}})(300 \text{ K}) \ln\left(\frac{40.0 \text{ dm}^3}{100 \text{ dm}^3}\right)$$

$$= -11400 \text{ J} = -11.4 \text{ kJ}$$

19-7

a) $2.25 \text{ L} @ 1.33 \text{ bar} \rightarrow 1.50 \text{ L} @ 2.00 \text{ bar}$

where $P_{\text{ext}} = 2.00 \text{ bar}$

$$W = -P_{\text{ext}} \Delta V = -2.00 \text{ bar} (1.50 - 2.25) = 1.5 \text{ bar} \cdot \text{L} = 150 \text{ J}$$

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

$P_{\text{ext}} = 3.75 \text{ bar}$

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

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

c) See bottom page 5.

19-40 (see Ex 19-11) $CCl_4(l) \rightarrow CCl_4(g)$

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

$$= -102.9 - (-135.44)$$

$$= 32.5 \text{ kJ/mol}$$

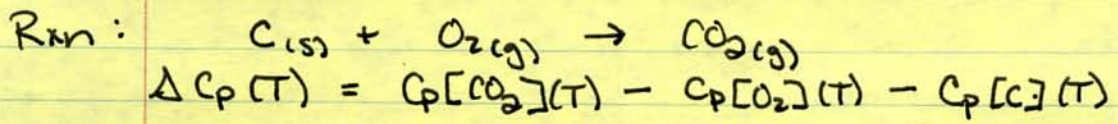
19-44

Eq 19.57

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

$$T_1 = 298 \text{ K} \quad \Delta_r H^\circ(298) = -393.509 \text{ kJ/mol}$$

$$T_2 = 1000 \text{ K}$$



$$\frac{\Delta C_p(T)}{R} = \left(\begin{array}{l} 2.593 + 7.661 \times 10^{-3} T - 4.78 \times 10^{-6} T^2 + 116 \times 10^{-9} T^3 \\ - 3.094 - 1.561 \times 10^{-3} T + 4.65 \times 10^{-7} T^2 \\ - (-0.6366) - 7.049 \times 10^{-3} T + 5.20 \times 10^{-6} T^2 - 1.38 \times 10^{-9} T^3 \\ \hline 0.1356 - 9.49 \times 10^{-4} T + 8.85 \times 10^{-7} T^2 - 2.2 \times 10^{-10} T^3 \end{array} \right)$$

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

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

$$R [-98.9 - (5.64)]$$

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

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

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

19-7c

$$w_{rev} = -nRT \ln(V_2/V_1)$$

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

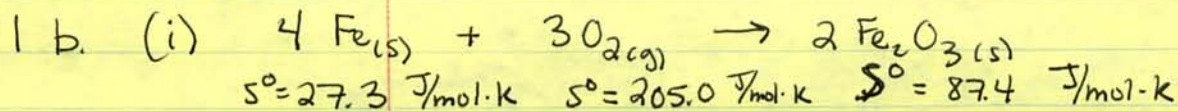
$$= -310.2 \text{ J}$$

* ideal gas $nRT = PV^*$
 choose 1 set... $(2.25 \text{ L})(1.33 \text{ bar})$
 $= 3 \text{ L}\cdot\text{bar}$
 $= 300 \text{ J}$

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

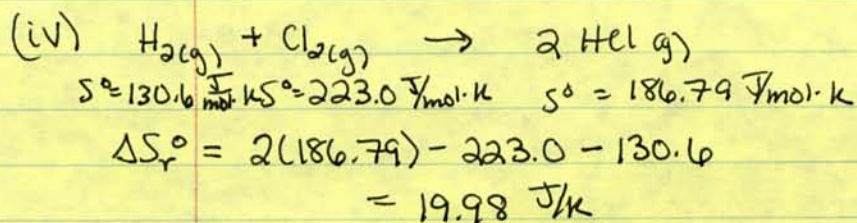
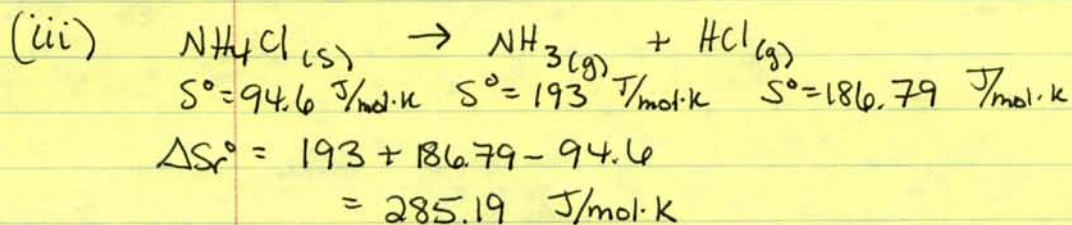
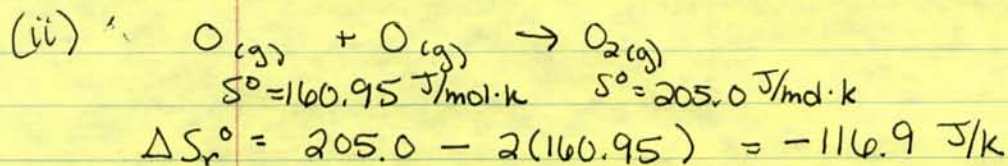
Ch20

1 a	(i)	-	Products reactants more ordered
	(ii)	-	"
	(iii)	+	reactants more ordered
	(iv)	+	"



$$\Delta S_r^\circ = 2(87.4) - 3(205.0) - 4(27.3)$$

$$= -549.4 \text{ J/K}$$



20-8

(8)

1 mol of ideal gas expanded reversibly + isothermally
from 10.0 dm³ to 20.0 dm³
↑
ΔT = 0
∴ du = 0

$$\delta q_{rev} = -\delta w_{rev}$$

$$\delta w_{rev} = -PdV$$
$$w_{rev} = -\int PdV = -\int_{10}^{20} \frac{nRT}{V} dV$$
$$= -nRT \ln \frac{20}{10}$$

$$q_{rev} = nRT \ln \frac{20}{10}$$

$$\Delta S = q_{rev}/T = nR \ln \frac{20}{10} = 5.76 \text{ J/mol K}$$

ΔS is positive b/c gas is expanding.

20-13

Show $\Delta S = C_p \ln T_2/T_1$ if C_p is independent of T

ΔS is a state function ... you can choose any path to calculate it.

I choose constant pressure reversible process.

$$\delta q_p = \Delta H = C_p(T) dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta q_{rev}}{T} = C_p \ln(T_2/T_1)$$

Find ΔS of 2.00 mol H₂O(l) if $\bar{C}_p = 75.2 \text{ J/K}\cdot\text{mol}$ +
 $T_2 = 90^\circ\text{C}$ + $T_1 = 10^\circ\text{C}$.
 $= 363 \text{ K}$ $T_1 = 283 \text{ K}$

$$\Delta S = n\bar{C}_p \ln(T_2/T_1) = (2.00 \text{ mol})(75.2 \text{ J/K}\cdot\text{mol}) \ln\left(\frac{363}{283}\right)$$
$$= 37.4 \text{ J/K}$$

20-18

Pressure constant, reversible process

$$q_{rev,P} = \Delta H_{vap} = n \Delta \bar{H}_{vap} \quad 100^\circ\text{C} = 373\text{ K}$$

$$\Delta S_{vap} = \frac{q_{rev}}{T} = \frac{n \Delta \bar{H}_{vap}}{T} = \frac{(2.00 \text{ mol})(40.65 \text{ kJ/mol})}{373 \text{ K}} = 0.21796 \text{ kJ/K}$$

or 217.96 J/K

ΔS_{vap} is positive b/c gas is more disordered than liquid.

20-25

Find ΔS_{sys} , ΔS_{surr} + ΔS_{tot} if $n=1$ mol ideal gas expanded isothermally + reversibly from 10 bar to 2 bar @ 300 K.

ΔS_{sys}

$$\begin{aligned} du &= 0 & \delta q &= \delta w \\ \delta w &= -P dV \\ w &= - \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= -nRT \ln V_2/V_1 \\ q &= nRT \ln V_2/V_1 \end{aligned}$$

$$\Delta S_{sys} = \frac{q}{T} = nR \ln V_2/V_1$$

For isothermal ideal gas ... $P_1 V_1 = P_2 V_2$
 $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$\begin{aligned} \Delta S_{sys} &= \frac{q}{T} = nR \ln (P_1/P_2) \\ &= (1 \text{ mol})(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(\ln(\frac{10}{2})) \\ \Delta S_{sys} &= 13.4 \text{ J/K} \end{aligned}$$

$\Delta S_{tot} = 0$ (reversible expansion) ↙ see pg 820 M+S

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 0$$

$\therefore \Delta S_{surr} = -13.4 \text{ J/K}$

20-29

$$\Delta \bar{S}_{mix} = -R \sum_{j=1}^N y_j \ln y_j \quad \text{where } y_j = \text{mol fraction}$$

$$y_{N_2} = \frac{2}{2+1} = 2/3$$

$$y_{O_2} = \frac{1}{2+1} = 1/3$$

$$\Delta \bar{S}_{mix} = -R \left(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3} \right) \quad R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$= 5.29 \text{ J/K}$$

20-40

$$\bar{S} = \frac{5}{2} R + R \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{\bar{V}}{N_A} \right] \quad \text{assume ideal gas}$$

use SI units...
kg, K, m, J

$$T = 298.2 \text{ K}$$

$$P = 1 \text{ bar}$$

$$m_{Kr} = 83.80 \text{ g/mol} = 1.39 \times 10^{-25} \text{ kg}$$

$$k_B = 1.3806 \times 10^{-23} \text{ J/K}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\bar{V} = \frac{RT}{P} = \frac{(0.08314 \frac{\text{dm}^3 \cdot \text{bar}}{\text{K}\cdot\text{mol}})(298.2 \text{ K})}{1 \text{ bar}}$$

$$= 24.79 \text{ dm}^3/\text{mol}$$

$$= 0.02479 \text{ m}^3/\text{mol}$$

$$\bar{S} = \frac{5}{2} R + R \ln \left[\frac{(2\pi (1.39 \times 10^{-25}) (1.3806 \times 10^{-23}) (298.2))^{3/2}}{(6.626 \times 10^{-34})^2} \cdot \frac{0.02479 \frac{\text{m}^3}{\text{mol}}}{6.022 \times 10^{23} \frac{1}{\text{mol}}} \right]$$

units: m⁻³

$$\bar{S} = \frac{5}{2} R + 17.23 R$$

$$= 19.73 R$$

$$= 164.07 \text{ J/K}\cdot\text{mol} \quad \leftarrow \text{same as experimental}$$