①

HWK #3

1a (i)

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

	$Ba(OH)_2 \cdot 8H_2O_{(s)}$	$2NH_4NO_{3(s)}$	$2NH_{3(aq)}$	$10H_2O_{(l)}$	$Ba(NO_3)_2$
ΔH_f kJ/mol	-3342	-365.6	-80.29	-285.83	-992.07
ΔS_{298} J/mol·K	427	151.1	111	69.91	214

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

$\boxed{\text{Endothermic}}$

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

(iii)

$$\Delta S_{rxn} = 214 + 10(69.91) + 2(111) - 2(151.1) - 427 = 405.9\ J/mol\cdot K$$
$$= 0.4059\ kJ/mol\cdot K$$

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

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

b (i)

$$C_{12}H_{22}O_{11} + \cancel{12O_2} \rightarrow \cancel{12CO_2} + 11H_2O \qquad \Delta H_{comb} = -5640.9\,\frac{kJ}{mol}$$
$$12\,\cancel{CO_2} \rightarrow \cancel{12O_2} + 12\,C(\text{graphite}) \qquad \Delta H = -\Delta H_f = 4722\,\frac{kJ}{mol}$$

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

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

$\boxed{\text{Exothermic}}$

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

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

Heat evolved : ~188 kJ

(iii) density $H_2SO_4 \cdot nH_2O$: 1.84 g/mL

$$(70\,\cancel{mL})(1.84\,\cancel{g}/\cancel{mL})\left(\frac{1\ mol}{98.07\cancel{g}}\right) = 1.31\ mol$$
$$(-40.58\ kJ/mol)(1.31\ mol) = -53.3\ kJ$$

Heat evolved : ~53 kJ

(iv) 188 + 53 = 241 kJ heat evolved

(2 below)

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

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

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

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

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

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

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

$P \neq$ constant

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

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

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

$$= -0.176\, \frac{V^2}{2}\Big|_{V_1}^{V_2}$$

$V_2 = \cancel{x}\ 22.70\ dm^3$, $V_1 = \cancel{x}\ 11.35\ dm^3$

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

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

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

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

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

$$= 17.0\ kJ$$

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

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

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

4a) Adiabatic : $\delta q = 0 \qquad dU = \delta w \qquad dU = n\bar{C}_V\,dT = \delta w$

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

$$\cancel{n}\bar{C}_V\,dT = -\cancel{n}\frac{RT}{V}\,dV$$

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 $\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{R/\bar{C}_V}$ QED.

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

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

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

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

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

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

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

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

5 ~~4.3~~. M+S problems

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

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

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

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

19-6

minimum amt work = reversible compression

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

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

$$= -11400\,J = -11.4\,kJ$$

19-7

a) 2.25 L @ 1.33 bar → 1.50 L @ 2.00 bar

where $P_{ext} = 2.00$ bar

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

b) 1.50 L @ 200 bar → 0.800 L @ 3.75 bar

$P_{ext} = 3.75$ bar

$$w = -P_{ext}\Delta V = -3.75\,bar(0.800 - 1.50) = 2.63\,bar\cdot L = 263\,J$$

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

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

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

$T_1 = 298$ K $\qquad \Delta_r H^\circ(298) = -393.509$ kJ/mol

$T_2 = 1000$ K

Rxn: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

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

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

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

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

$$R[-98.9 - (5.64)]$$
$$= (8.314 \text{ J/K·mol})(-104.54 \text{ K}) = -869.2 \text{ J/mol}$$

$$\Delta_r H(1000 \text{ K}) = -393.509 \text{ kJ/mol} - 0.8692 \text{ kJ/mol}$$
$$= -394.38 \text{ kJ/mol}$$

19-7 c

$$w_{rev} = -nRT\ln(V_2/V_1)$$
$$= -300 \text{ J} \ln(0.8/2.25)$$
$$\boxed{= -310.2 \text{ J}}$$

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

* ideal gas $nRT = PV$ *

choose 1 set… $(2.25 \text{ L})(1.3\bar{3} \text{ bar})$

$= 3$ L·bar

$= 300$ J

Ch20

1a (i\ − Products ~~reactants~~ more ordered
(ii) − "
(iii) + reactants more ordered
(iv) + "

1 b. (i) $4\ Fe_{(s)} + 3O_{2(g)} \rightarrow 2\ Fe_2O_{3(s)}$
$S^\circ = 27.3$ J/mol·K $S^\circ = 205.0$ J/mol·K $S^\circ = 87.4$ J/mol·K

$\Delta S_r^\circ = 2(87.4) - 3(205.0) - 4(27.3)$
$= -549.4$ J/K

(ii) $O_{(g)} + O_{(g)} \rightarrow O_{2(g)}$
$S^\circ = 160.95$ J/mol·K $S^\circ = 205.0$ J/mol·K
$\Delta S_r^\circ = 205.0 - 2(160.95) = -116.9$ J/K

(iii) $NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$
$S^\circ = 94.6$ J/mol·K $S^\circ = 193$ J/mol·K $S^\circ = 186.79$ J/mol·K
$\Delta S_r^\circ = 193 + 186.79 - 94.6$
$= 285.19$ J/mol·K

(iv) $H_{2(g)} + Cl_{2(g)} \rightarrow 2\ HCl\ g)$
$S^\circ = 130.6\ \frac{J}{mol}\cdot K$ $S^\circ = 223.0$ J/mol·K $S^\circ = 186.79$ J/mol·K
$\Delta S_r^\circ = 2(186.79) - 223.0 - 130.6$
$= 19.98$ J/K

Chapter 20

2. a. Ar ... it has a greater mass
   b (i) CO_2 "
   (ii) D_2O "
   (iii) Ethane " and it has more vibrational DOF

3. $\boxed{20\text{-}6}$ (Ideal gas)

Fig 20.3

Two step process: ① P_1, V_1, T_1 to P_2, V_1, T_4 rev. cooling @ constant V_1
② P_2, V_1, T_4 to P_2, V_2, T_1 reversible ex. @ constant P_2

Step 1

$P_1, V_1, T_1 \rightarrow P_2, V_1, T_4$ no work b/c V_1 is constant

$$dU = \delta q_{rev} = C_V(T)\,dT$$

$$q_{rev,1} = \int_{T_1}^{T_4} C_V(T)\,dT \qquad \Delta S_1 = \int \frac{\delta q_{rev}}{T}$$

$$\Delta S_1 = \int_{T_1}^{T_4} \frac{C_V(T)}{T}\,dT$$

Step 2

$P_2, V_1, T_4 \rightarrow P_2, V_2, T_1$

$$\delta q_{rev} = dU - \delta w_{rev} \qquad \delta w_{rev} = -P\,dV$$

$$= C_V(T)\,dT + P_2\,dV$$

$$q_{rev,2} = \int_{T_4}^{T_1} C_V(T)\,dT + \cancel{P_2}\int_{V_1}^{V_2} P_2\,dV$$

$$\Delta S_2 = \int_{T_4}^{T_1} \frac{C_V(T)\,dT}{T} + \int_{V_1}^{V_2} \frac{P_2}{T}\,dV \qquad \frac{P_2}{T} = \frac{nR}{V}$$

$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1}$$

- q is different from paths A, B+C and D+E but ΔS_{Tot} is the <u>same</u>.

20-8 1 mol of ideal gas expanded reversibly + isothermally from 10.0 dm^3 to 20.0 dm^3

$\uparrow$ $\Delta T = 0$

$\therefore dU = 0$

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

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

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

$$= -nRT \ln \frac{20}{10}$$

$$q_{rev} = nRT \ln {}^{20}/_{10}$$

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

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.

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

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

Find ΔS of 2.00 mol $H_2O_{(l)}$ if $\overline{C}_p = 75.2$ J/K·mol + $T_2 = 90°C$ + $T_1 = 10°C$.

$= 363 K$ $\quad T_1 = 283 K$

$$\Delta S = n\overline{C}_p \ln({}^{T_2}/_{T_1}) = (2.00 \text{ mol})(75.2 \tfrac{J}{K \cdot mol}) \ln\left(\tfrac{363}{283}\right)$$

$$= 37.4 \text{ J/K}$$

20-18 Pressure constant, reversible process

$$q_{rev,P} = \Delta H_{vap} = n\Delta \overline{H}_{vap}$$ 100°C = 373 K

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

or 217.96 J/K

ΔS_{vap} is positive b/c gas is more disordured 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}

$dU = 0$ $\quad \delta q = \delta w$

$$\delta W = -P\,dV$$

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$

$$= -nRT \ln V_2/V_1$$

$$q = nRT \ln V_2/V_1$$

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

For isothermal ideal gas ... $P_1V_1 = P_2V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\Delta S_{sys} = \frac{q}{T} = nR \ln (P_1/P_2)$$

$$= (1\ mol)(8.314\ \tfrac{J}{mol \cdot K})(\ln(\tfrac{10}{2}))$$

$$\Delta S_{sys} = 13.4\ J/K$$

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

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

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

20-29

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

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

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

$$\Delta\overline{S}_{mix} = -R\left(\tfrac{2}{3}\ln 2/3 + \tfrac{1}{3}\ln 1/3\right)$$ $R = 8.314$ J/mol·K

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

20-40

$$\overline{S} = \frac{5}{2}R + R\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\overline{V}\,\overset{1}{g_{el}}}{N_A}\right]$$ assume ideal gas

use SI units… kg, K, m, J

$T = 298.2$ K

$P = 1$ bar

$m_{Kr} = 83.80$ g/mol = ~~0.0838 kg/mol~~ 1.39×10^{-25} kg

$k_B = 1.3806\times10^{-23}$ J/K

$h = 6.626\times10^{-34}$ J·s

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

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

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

$$\overline{S} = \frac{5}{2}R + R\ln\left[\overset{\swarrow \text{units}: \text{m}^{-3}}{\left(\frac{2\pi(1.39\times10^{-25})(1.3806\times10^{-23})(298.2)}{(6.626\times10^{-34})^2}\right)^{3/2}} \cdot \frac{0.02479\ \frac{\text{m}^3}{\cancel{\text{mol}}}}{6.022\times10^{23}\ \frac{1}{\cancel{\text{mol}}}}\right]$$

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

$$= 19.73R$$

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