HW 1 KEY

CH1

D 1.3

$$z = \frac{PV_m}{RT}$$

$$z = \frac{V_{actual}}{V_{ideal}}$$

As pressure increases, $z > 1$, molecules are colliding more often, intermolecular repulsive forces dominate, and $V_{real\,gas} > V_{ideal\,gas}$. At low pressures, $z \approx 1$ and gases tend to exhibit ideal behavior, no intermolecular forces. At intermediate pressures, $z < 1$ because attractive forces will dominate and $V_{real} < V_{ideal}$.

E 1.2

a) $P_1 V_1 = P_2 V_2$

$V_2 = 4.65 \, dm^3$ 　　 $P_2 = 5.04 \, bar$

$V_1 = (4.65 + 2.20) dm^3$

$P_1 = \frac{4.65 \, dm^3}{6.85 \, dm^3} (5.04 \, bar)$

$P_1 = 3.42 \, bar$

$P_1 = 3.42 \, bar \left| \dfrac{1 \, atm}{1.013 \, bar} \right. = 3.38 \, atm$

E 1.13 a

a) $P = \dfrac{nRT}{V}$

$n = 1$, $T = 273.15 \, K$ (i) or $1000 \, K$ (ii)

$V = 22.414 \, dm^3$ (i) or $100 \, cm^3$ (ii)

Remember, $dm^3 = L$

$$P = \frac{(1 \, mol)(0.08206 \, L \, atm \, K^{-1} mol^{-1})(273.15 \, K)}{22.414 \, L} = 1.0 \, atm : i$$

Same work for ii: $P = 820 \, atm$

Since $100 \, cm^3 = 0.100 \, dm^3 = 0.100 \, L$

E 1.18 a   Dalton's Law of Partial Pressures

a) $n_{total} = n_{H_2} + n_{N_2} = 3$ mol

$\quad\quad n_{H_2} = 2$ mol $\quad\quad n_{N_2} = 1$ mol

$\quad X_{H_2} = \dfrac{2 \text{ mol}}{3 \text{ mol}} = 0.667 \quad\quad X_{N_2} = 0.333$

b) $P_i = X_i \, P_{total}$

$$P_{total} = \frac{n_{total} \, RT}{V}$$

$\Rightarrow$ Ideal gas law holds for individual component gases

$$P_{H_2} = \frac{2 \text{ mol} \,(0.082056 \text{ Latm K}^{-1}\text{mol}^{-1})(273.15 \text{ k})}{22.4 \text{ L}}$$

$\quad\quad P_{H_2} = 2.0$ atm

$\quad\quad P_{N_2} = \dfrac{P_{H_2}}{2} = 1$ atm

c) $P_{total} = \sum_i P_i = P_{H_2} + P_{N_2} = 3$ atm

E 1.22 a

Solve VDW equation for b:

$$b = V_m - \frac{RT}{\left(P + \dfrac{a}{V_m^2}\right)} = \frac{5 \times 10^{-4} \, m^3}{mol} - \frac{8.314 \, J\,K^{-1}mol^{-1} \cdot 273 \, k}{\left[3 \times 10^{6} \, Pa + \left(\dfrac{0.5 \, m^6 Pa \, mol^{-2}}{(5 \times 10^{-4} m^3 mol^{-1})^2}\right)\right]}$$

$b = 0.46 \times 10^{-4} \, m^3 \, mol^{-1}$

E1.22a cont.

$$z = \frac{PV}{nRT} = \frac{PV_m}{RT} = \frac{(3 \times 10^6 \text{ Pa})(5 \times 10^{-4} \text{ m}^3)}{(8.314 \text{ J K}^{-1}\text{mol}^{-1})(273k)} = 0.66$$

N1.23   T = 298 K   P = 1 atm

$$2.2990 \text{ g} \left| \frac{1 \text{ mol } N_2}{28.02 \text{ g}} \right. = 0.08205 \text{ mol } N_2$$

Mixture: $(2.3102 - 2.2990)$ g   = 0.0112 g Ar

$$0.0112 \text{ g Ar} \left| \frac{1 \text{ mol Ar}}{37.95 \text{ g}} \right. = 2.8 \times 10^{-4} \text{ mol Ar}$$

$$X_{Ar} = \frac{2.8 \times 10^{-4} \text{ mol Ar}}{(2.8 \times 10^{-4} + 0.08205) \text{ mol total}} = \cancel{0.003} \; 0.003$$

CH2

D2.3

$\Delta u = q + w$ (heat + work), and the total energy change of the system. Enthalpy is heat transfer, and $\Delta H = U + pV$, which is heat transfer at constant pressure, p (thus, $\Delta H = q_p$).
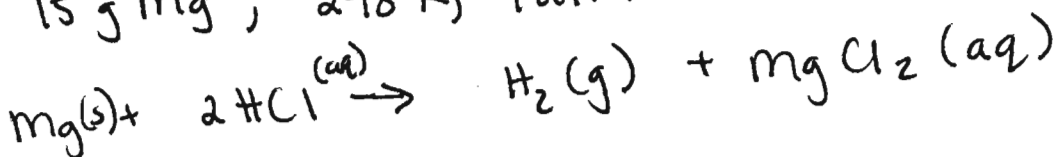
E2.2a

Expansion against constant pressure

$$w = -P_{ex} \Delta V \qquad P_{ex} = 1 atm \left(\frac{1.01 \times 10^5 Pa}{1 atm} \right) = 1.01 \times 10^5 Pa$$

$$\Delta V = 100 cm^2 (10 cm) = 1000 cm^3 \left| \left(\frac{10^{-2}}{C} \right)^3 \right. = 10^{-3} m^3$$

$$w = -(1.01 \times 10^5 Pa)(10^{-3} m^3) = \boxed{-101 J = w}$$

E2.7a

15 g Mg, 298 K, 1 atm

$$Mg(s) + 2 HCl^{(aq)} \longrightarrow H_2(g) + Mg Cl_2 (aq)$$

$$V_i (H_2) = 0$$

$$V_f = \frac{n(H_2) RT}{P} = \frac{\left(15 g \left| \frac{1 mol\, Mg}{24.312} \right. \left| \frac{1 mol\, H_2}{1 mol\, Mg} \right. \right) \left(\frac{.08206\, L\, atm}{K\, mol} \right) (298 K)}{1 atm}$$

$$V_f = \cancel{9.5 mol} 15.08 L$$

$$-1520 J$$

$$w = -P_{ext} \Delta V = -1 atm (9.87 - 0) L = -9.87 L\, atm \left(\frac{101.3 J}{1 atm\, L} \right) = \cancel{}$$

Sorry, poor use of calculator: $\boxed{w = -1.5 KJ}$

E2.16 a

$\Delta H^\circ_{vap} = 26.0 \text{ kJ/mol}$, 0.50 mol , $T = 250 \text{ K}, P = 750 \text{ torr}$

Want: $q, w, \Delta H, \Delta U$

Constant pressure:

$$\underline{q_p} = \Delta H = n \Delta H_{vap} \, T_f = (0.50 \text{ mol})(26 \text{ kJ/mol})(250 \text{ K})$$
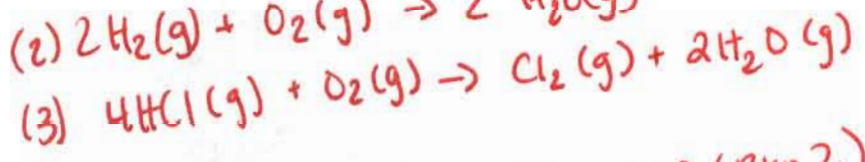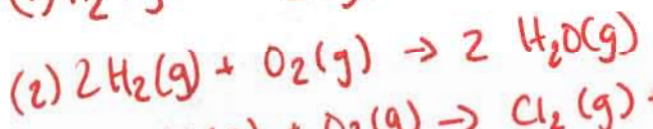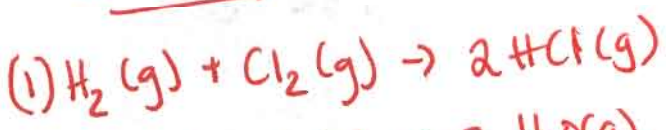
$$q_p = 13.0 \text{ kJ} = \Delta H$$

$$\underline{w} = -P_{ext} \, \Delta V = -P_{ext} V_f \cancel{\text{XXXX}} = -nRT = -(0.50 \text{ mol})\left(\frac{8.314 \text{ J}}{\text{K mol}}\right)(250 \text{ K})$$

$$w = -1.0 \text{ kJ}$$

$$\underline{\Delta U} = q + w = 13 \text{ kJ} - 1 \text{ kJ} = 12 \text{ kJ}$$

~~E2.22 a~~

E 2.22 a

(1) $H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$

(2) $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$

(3) $4 HCl(g) + O_2(g) \rightarrow Cl_2(g) + 2 H_2O(g)$

$$\Delta_f H^\circ = -2 \Delta_r H^\circ (Rxn \, 1) + \Delta_r H^\circ (Rxn \, 2) = -2(-184.62) + (-483.64) = -114.4 \frac{kJ}{mol}$$

$$\Delta_r U^\circ = \Delta_r H^\circ - \Delta n_g RT = (-114.4 \text{ kJ/mol}) - (-1)(298 \text{K})(8.314 \text{ J K}^{-1} \text{mol}^{-1})$$

$$\Delta n_g = -1 \qquad \Delta_r U^\circ = -111.92 \text{ kJ/mol}$$

b) $\Delta_f H (\text{molecule}) = \dfrac{\Delta_r H^\circ (\text{molecule})}{\sqrt{\text{molecule}}}$

$$\Delta_f H (HCl(g)) = \frac{-184.62 \text{ kJ mol}^{-1}}{2} = -92.31 \text{ kJ mol}^{-1}$$

$$\Delta_f H (H_2O(g)) = \frac{-483.64}{2} = -241.82 \text{ kJ mol}^{-1}$$

E 2.27a $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

$$SO_4^{2-} \rightarrow \text{spectator ion}$$

$$\Delta H^\circ = \sum_{prod} v_i H_i^\circ - \sum_{react.} v_i H_i^\circ = -218.66 \; kJ/mol$$

N2.1

1) $T_1 = \dfrac{PV_1}{nR} = \dfrac{(1\,atm)(22.44L)}{0.08206 \; Latm\,K^{-1}mol^{-1}} = 273.46\,K = T_1$

2) Same way, $T_2 = 2T_1 \quad \cancel{\text{...}} = 546.92K = T_2$

3) $P_3 = \frac{1}{2}P_1, \quad V_3 = 2V_1, \quad T_3 = T_1 = 273.46\,K$ (along isotherm)

Let's consider all steps to be reversible:

Step 1-2 $w = -P_{ext}\Delta V = -nR\Delta T = (-1mol)(8.314 J\,K^{-1}mol^{-1})(273K) = -2.27\,kJ$

$\Delta u = nC_{V,m}\Delta T = (1\,mol)(\frac{3}{2}R)(273\,K) = 3.4\,kJ$

$q = \Delta u - w = 3.40\,kJ - (-2.27\,kJ) = 5.67 \times 10^3\,J$

$\Delta H = q_p = 5.67\,kJ$

Step 2→3   Constant V, $w = 0$

$q_v = \Delta u = nC_{V,m}\Delta T = (1\,mol)(\frac{3}{2}R)(-273\,K) = -3.40\,kJ$

ALSO: $\Delta u_{tot} = 0$, so $\Delta u_1 = -\Delta u_2$, since $\Delta u_3 = 0$ (isotherm)

Since $\Delta H \equiv \Delta u + \Delta(PV) = \Delta u + \Delta(nRT) = \Delta u + nR\Delta T$

Here, $\Delta T = -273$, $\Delta H = -5.67 \times 10^3 J = -5.67\,kJ$

Step 3→1 $\Delta u = 0 = \Delta H$, along isothermal process in I.G.

$-q = w = -nRT \ln\dfrac{V_1}{V_3} = -(1mol)(8.314)(273K)\ln\left(\frac{1}{2}\right)$

$-q = 1.57\,kJ \qquad q = -1.57\,kJ$

	q(kJ)	w(kJ)	Δu	ΔH
Step 1→2	5.67	-2.27	3.40	5.67
2→3	-3.40	0	-3.40	-5.67
3→1	-1.57	1.57	0	0
Cycle	0.70	-0.70	0	0

DR. VDB's problems:

1) $8.314 \, J \, K^{-1} mol^{-1}$, $J = Pa \, m^3$, $1 Pa = 10^{-6} MPa$

$\dfrac{8.314 \, m^3 Pa}{mol \, K} \left| \dfrac{10^{-6} cm^3}{m^3} \right| \dfrac{MPa}{10^{6} Pa} = \dfrac{8.314 \, cm^3 MPa}{mol \cdot K}$

$1 cm^3 = 1 mL = 2.6 \times 10^{-4}$ gallons

$14.5 \, bar = 1 \, psi$

$\dfrac{8.314 \, cm^3 MPa}{mol \, K} \left| \dfrac{1 mL}{cm^3} \right| \dfrac{2.6 \times 10^{-4} gal}{1 mL} \left| \dfrac{1 \, psi}{145 \, MPa} \right. = \dfrac{1.5 \times 10^{-5} \, gal \cdot psi}{mol \cdot K} = R$

2) a. ΔV (potential energy) $= mg\Delta h$

$\qquad = (50 \, kg)(9.8 \, m s^{-2})(1m) = 490 \, kg \, m^2 s^{-2} = 490 \, J$

b. $C + O_2 \rightarrow CO_2 \quad \Delta H = 393 \, kJ/mol$

$\dfrac{1 g \, C}{} \left| \dfrac{1 mol \, C}{12 g \, C} \right| \dfrac{393 \, kJ}{1 mol \, C} = 3.28 \times 10^{34} \, J \quad (k = 10^3)$

c. $\dfrac{1840 \, kcal}{} \left| \dfrac{10^3}{k} \right| \dfrac{4.184 \, J}{1 \, cal} = 7.7 \times 10^6 \quad J$

d. $100 \, W = \dfrac{100 J}{s} \left| \dfrac{3600 \, s}{1 \, hr} \right| \dfrac{24 hr}{} = 8.64 \times 10^6 \, J/day$

3) $C_{V,M} = 1.5R \quad P_2 = 100 \, bar \quad P_1 = 10 \, bar \quad T = 300 \, K \quad n = 2$

Constant T, $P_1 = 100$, $P_2 = 10 \, bar$

$\Delta U = q + w$

Find $\Delta U, w, q$, and what if reversibly

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

$PV = nRT$

$PV_f = n_f RT$

so $V_f = \dfrac{n_f RT}{P_f}$ → same expression for initial volume

$n_i = n_f$

$w = -P_f \Delta V = -P_f \left(\dfrac{n_f RT}{P_f} - \dfrac{n_i RT}{P_i} \right) = \left(nRT - \dfrac{nRT P_f}{P_i} \right)$

$w = -nRT \left(1 - \dfrac{P_f}{P_i} \right) = 2 \, mol \cdot 8.314 \, J \, K^{-1} mol^{-1} \cdot 300 K \left(1 - \dfrac{100 \, bar}{10 \, bar} \right) = \boxed{4.48 \times 10^4 \, J = w}$

3) continued

Found work, $\omega = 4.48 \times 10^4$ J

$\Delta U = 0 = q + \omega$, so $q = -\omega = -4.48 \times 10^4$ J

Internal energy, U, is a state function, $\Delta U = U_f - U_i$ and $U_f = U_i$

cyclic process

$\Delta U = C\Delta T, \Delta T = 0$

Reversible process:

isothermal

$$\omega = -nRT \ln\left(\frac{V_f}{V_i}\right) \quad \text{if ideal,} \quad \omega = -nRT \ln\left(\frac{P_i}{P_f}\right)$$

Just care about ratio

Step 1:

~~202 24Acoles 317J not 3K~~

$$\omega_1 = -nRT \ln\left(\frac{10}{100}\right)$$

Step 2:

$$\omega_2 = -nRT \ln\left(\frac{100}{10}\right)$$

overall, $\omega_{tot} = \omega_1 + \omega_2 = -nRT \ln\left(\frac{10}{100}\right) + nRT \ln\left(\frac{10}{100}\right) = 0$

OR: $\omega_{tot} = -nRT \ln\left(\frac{P_i}{P_f}\right)^{0}$, $P_i = P_f$ @ $0 = \omega_{total}$

$$\Delta U = 0 = q + \omega = q + 0$$

$$\therefore q = \omega = 0$$

4. $W = -\int_{V_1}^{V_2} P\,dV = -\int \frac{RT}{V_m-b} - \frac{a}{TV_m^2}\,dV_m$

$= -\left[RT\ln(V_m-b)\Big|_{V_1}^{V_2} + \frac{a}{TV_m}\Big|_{V_1}^{V_2} \right]$

$= -\left[RT\left[\ln(V_2-b) - \ln(V_1-b)\right] + \frac{a}{T}\left[\frac{1}{V_2} - \frac{1}{V_1}\right]\right]$

where $R = 0.08314$ L bar k^{-1} mol^{-1}, $T = 300$k, $V_2 = \dfrac{10L}{224}$, $V_1 = \dfrac{4L}{22.4}$ L mol^{-1}

$a = 1080$ L^2 mol^{-1} $b = 0.04287$ L mol^{-1}

$W = -40.6$ Lbar/mol $= -4060$ J/mol

For isothermal, reversible expansion, ideal gas, $w = -q$, $\Delta u = 0$

5. $C_p = C_v + T\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P$

a. $P(V-nb) = nRT$ $\therefore$ $P = \dfrac{nRT}{V-nb}$

$V = \dfrac{nRT}{P} + nb$

$\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{nR}{V-nb}$ and $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{nR}{P}$

$C_p = C_v + T\left(\dfrac{nR}{V-nb}\right)\left(\dfrac{nR}{P}\right)$

$= C_v + \dfrac{PnR}{P} = \boxed{C_v + nR = C_p}$

7. $2Na(s) + 2H_2O(l) \rightarrow H_2(g) + 2Na^+(aq) + 2OH^-(aq)$

$\Delta H_f^\circ:$ 0 -285.83 0 -240.12 $-230 \; \frac{kJ}{mol}$
298K

$\Delta H_f^\circ:$
350K

$\Delta H_{rxn}^\circ = \sum_a \Delta H_i^\circ - \sum_a a \Delta H_i^\circ = [2(-240.12) + (-230)2] - [2(-285.83)] = -368.58 \frac{kJ}{mol}$
    products   reactants

$\Delta H_r(T_2) = \Delta H_r^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ \, dT$, where $\Delta_r C_p^\circ = \sum_{prod.} \upsilon \, C_{p,m}^\circ - \sum_{reactants} \upsilon \, C_{p,m}^\circ$

If C_p° is temperature independent, $\Delta H_r(T_2) = \Delta H_r^\circ(T_1) + \Delta_r C_p^\circ \Delta T$

$\Delta_r C_{p,m}^\circ = [28.82 + 2(46.4) + 2(-148.5)] - [2(-75.3) + 2(28.24)]$

All values for STP(thermo) and were found in text appendix, in J/Kmol

$\Delta_r C_p^\circ = -81.28 \; J/Kmol$

$\Delta H_r(350K) = \Delta H_r(298K) + \Delta_r C_p^\circ \Delta T = -368.58 + (-81.28 \frac{J}{Kmol})(52K)$
                                                $\frac{kJ}{mol}$

$\Delta H_f(350K) = -372.8 \; kJ/mol$

Work: Constant pressure $w = -P_{ext} \Delta V$

$1 atm \approx 101 J$ $V_i \approx 0, \; V_f = \frac{nRT}{P_{ext}} = \frac{\left(10g \, Na \left| \frac{1 mol \, Na}{23g} \right| \frac{1 mol \, H_2(g)}{2 mol \, Na}\right)(0.08206)(T)}{1 \, atm}$

$V_f(298K) = 5.31L \; ; \quad w \approx -531 J$

$V_f(350K) = 6.23L \; ; \quad w \approx -623 J$

For $0.217 \, mol \, H_2 (10g \, Na)$, $\Delta H = -368.58 \; kJ \, mol^{-1}(0.217) = -80 \, kJ$

magnitude of ΔH $>>$ magnitude work