

$$i) P = (1.0 \text{ mol}) (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) (1000 \text{ K}) = \boxed{8.2 \times 10^2 \text{ atm}}$$

$$ii) P = (1.0 \text{ mol}) (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) (273.15 \text{ K}) = \boxed{1.0 \text{ atm}}$$

$n = 1.0 \text{ mol}$   
 $T = 273.15 \text{ K}$   
 $T = 1000 \text{ K}$   
 $V = 2.414 \text{ dm}^3$   
 $V = 100 \text{ cm}^3 = 0.100 \text{ dm}^3$

$E 1.13a) PV = nRT, P = \frac{nRT}{V}$

$1 \text{ atm} = 1.013 \text{ bar}$   
 $\frac{3.42 \text{ bar}}{1 \text{ atm}} \Big| \frac{1 \text{ atm}}{1.013 \text{ bar}} = \boxed{3.38 \text{ atm}}$

$$P_i = \frac{P_f V_f}{V_i} = \frac{(5.04 \text{ bar})(6.85 \text{ dm}^3)}{(4.65 \text{ dm}^3 + 2.20 \text{ dm}^3)} = \boxed{3.42 \text{ bar}}$$

$P_f V_f = P_i V_i$   
 $V_i = 4.65 \text{ dm}^3 + 2.20 \text{ dm}^3 = 6.85 \text{ dm}^3$   
 $V_f = 4.65 \text{ dm}^3$   
 $P_f = 5.04 \text{ bar}$

Boyle's Law E 1.20

$$0.1.3) Z = \frac{P_m}{RT}$$

As pressure increases, molecules become closer together and Z increases (molecules repel).

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$$b) p = \frac{nRT}{V-nb} - \frac{an^2}{V^2} \quad \text{Van der Waals}$$

Use table 1.6:

$$a = 5.507 \text{ dm}^6 \text{ atm mol}^{-2}$$

$$b = 6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

$$i) p = \frac{(1.0 \text{ mol}) \left( \frac{2.08206 \text{ dm}^3 \text{ atm}}{3.0 \text{ mol}} T^{-1} \text{ mol}^{-1} \right) (273.15 \text{ K})}{22.414 \text{ dm}^3} - \frac{(1.0 \text{ mol}) \left( 6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \right)^2}{(22.414 \text{ dm}^3)^2} - \frac{(5.507 \text{ dm}^6 \text{ atm mol}^{-2}) (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2}$$

$$= 1.003 \text{ atm} - 1.11 \times 10^{-2} \text{ atm} = 1.0 \text{ atm}$$

$$ii) p = \frac{(1.0 \text{ mol}) \left( \frac{0.08206 \text{ dm}^3 \text{ atm}}{3.0 \text{ mol}} T^{-1} \text{ mol}^{-1} \right) (273.15 \text{ K})}{(0.100 \text{ dm}^3)} - \frac{(1.0 \text{ mol}) \left( 6.0651 \text{ dm}^3 \text{ mol}^{-1} \right)^2}{(0.100 \text{ dm}^3)^2} - \frac{(5.507 \text{ dm}^6 \text{ atm mol}^{-2}) (1.0 \text{ mol})^2}{(0.100 \text{ dm}^3)^2}$$

$$= 2.27 \times 10^2 \text{ atm} - 5.51 \times 10^2 \text{ atm} = \boxed{1.7 \times 10^2 \text{ atm}}$$

$$\text{E1.18a) } n_{\text{total}} = n(\text{H}_2) + n(\text{N}_2) = 2.0 \text{ mol} + 1.0 \text{ mol} = 3.0 \text{ mol}$$

$$a) x(\text{H}_2) = \frac{2.0 \text{ mol}}{3.0 \text{ mol}} = \boxed{0.67} \quad x(\text{N}_2) = \frac{1.0 \text{ mol}}{3.0 \text{ mol}} = \boxed{0.33}$$

$$b) p_{\text{H}_2} = n_{\text{H}_2} \frac{RT}{V} = \frac{(2.0 \text{ mol}) \left( \frac{0.08206 \text{ dm}^3 \text{ atm}}{22.4 \text{ dm}^3} T^{-1} \text{ mol}^{-1} \right) (273.15 \text{ K})}{22.4 \text{ dm}^3} = 2.0 \text{ atm}$$

$$p_{\text{N}_2} = \frac{(1.0 \text{ mol}) \left( \frac{0.08206 \text{ dm}^3 \text{ atm}}{22.4 \text{ dm}^3} T^{-1} \text{ mol}^{-1} \right) (273.15 \text{ K})}{22.4 \text{ dm}^3} = 1.0 \text{ atm}$$

$$c) \text{ Total pressure} = 2.0 \text{ atm} + 1.0 \text{ atm} = 3.0 \text{ atm}$$

F1.22a) a =  $0.50 \text{ m}^6 \text{ Pa mol}^{-2}$   
 $V = 5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$   
 $T = 273 \text{ K}$   
 $P = 3.0 \times 10^6 \text{ Pa}$

$$b = V_m - RT \left( \frac{p + \frac{a}{V_m^2}}{p} \right) = 5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} - (8.314 \text{ J K}^{-1}) (273 \text{ K}) \left( \frac{3.0 \times 10^6 \text{ Pa} + \frac{0.50 \text{ m}^6 \text{ Pa mol}^{-2}}{5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}}{3.0 \times 10^6 \text{ Pa}} \right)$$

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

$$Z = \frac{pV_m}{RT} = \frac{(3.0 \times 10^6 \text{ Pa}) (5.00 \times 10^{-4} \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K})} = 0.66$$

0.66 : attractive forces

M1.23) a) Assume room temperature and Latin, Nitrogen, moly.

$$\frac{2.29 \text{ g}}{28.02 \text{ g}} \Big| \frac{1 \text{ mol}}{28.02 \text{ g}} = 0.08205 \text{ mol}$$

$$PV = nRT$$

$$(10^5 \text{ Pa}) (V) = (0.08205 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})$$

$$V = 2.00 \text{ L}$$

Mixture of Nitrogen & Argon  
 $2.3102 \text{ g Total} - 2.29 \text{ g } N_2 = 0.0112 \text{ g Ar}$

0.0112 g Ar		1 mol	=	$2.80 \times 10^{-4} \text{ mol}$
39.95 g				

Total moles: 0.0823

Mole Fraction  $N_2$ :  $\frac{0.08205}{0.0823} \times 100\% = 99.7\%$

Mole Fraction Ar:  $\frac{2.80 \times 10^{-4} \text{ mol}}{0.0823 \text{ mol}} \times 100\% = 0.3\%$

0.2.3)  $\Delta U$  (change in internal energy) = heat + work  
 This is the total energy change in the system.

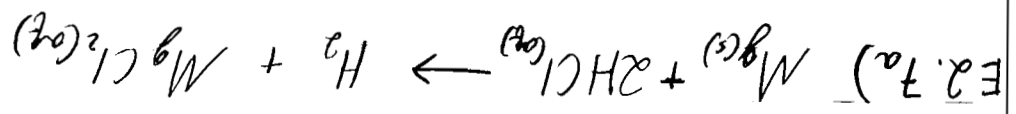
Enthalpy (heat transfer) =  $U + pV$ . The change in enthalpy is the heat transfer at constant pressure ( $\Delta H = q_p$ )

Then on a piston-cylinder, if there is no work done, in a closed system, the change in energy is assumed by the change in enthalpy.

E.2.2a) Expansion Against Constant Pressure

$W = -p_{ex} \Delta V$   
 $p_{ex} = 1.0 \text{ atm} = (1.013 \times 10^5 \text{ Pa}) (1.0 \text{ atm}) = 1.01 \times 10^5 \text{ Pa}$

$\Delta V$  is the change in volume (cross sectional area  $\times$  displacement)  
 $\Delta V = 100 \text{ cm}^2 \times 10 \text{ cm} = 1000 \text{ cm}^3 \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 = 1.0 \times 10^{-3} \text{ m}^3$   
 $W = -p_{ex} \Delta V = -1.01 \times 10^5 \text{ Pa} \times 1.0 \times 10^{-3} \text{ m}^3 = -1.01 \times 10^2 \text{ J}$



Work is done on atmosphere by  $\text{H}_2$  gas  
 $V_f + H_f \text{ gas} = \phi = V_f + V_f$   
 $W_f = -p_{ex} \Delta V = -p_{ex} V_f = -p_{ex} \left(\frac{nRT}{p_{ex}}\right) = -nRT$

$n = \frac{15 \text{ g}}{24.312 \text{ g/mol}} = 0.617 \text{ mol}$

$W = -0.617 \text{ mol} \cdot 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298.15 \text{ K} = -1529.9 \text{ J} = \boxed{-1.5 \text{ kJ}}$

E2.16a) Constant Pressure: Calculate  $q$ ,  $w$ ,  $\Delta H$ ,  $\Delta U$

$$q = \Delta H = n \Delta_{vap} H^\circ_f = (0.50 \text{ mol}) (26.0 \text{ kJ mol}^{-1}) = \boxed{13.0 \text{ kJ}}$$

$$w = -p \Delta V, \quad V_f - V_i = \Delta V$$

$$w = -p V_f = -nRT = -(0.50 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (250 \text{ K})$$

$$w = -1039 \text{ J} = \boxed{-1.0 \text{ kJ}}$$

$$\Delta U = w + q = 13.0 \text{ kJ} - 1.0 \text{ kJ} = \boxed{12.0 \text{ kJ}}$$

Assume that the external pressure does not affect the final volume.

E2.22a)  $\Delta_r H^\circ = -2 \times \text{reaction (1)} + \text{reaction (2)}$

$$\Delta_r H^\circ = -2(-184.62 \text{ kJ mol}^{-1}) + (-483.64 \text{ kJ mol}^{-1})$$

$$= \boxed{-114.40 \text{ kJ mol}^{-1}}$$

$$\Delta_r U^\circ = \Delta_r H^\circ - \Delta n_g RT, \quad \Delta n_g = -1$$

$$= (-114.40 \text{ kJ mol}^{-1}) - (-1)(2.48 \text{ kJ mol}^{-1})$$

$$= \boxed{-111.92 \text{ kJ mol}^{-1}}$$

b)  $\Delta_r H^\circ (\text{molecule}) = \Delta_r H^\circ (\text{molecule}) \cdot \nu$ ;  $\nu = \text{stoichiometric coefficient}$

$$\Delta_r H^\circ (HCl(g)) = -184.62 \text{ kJ mol}^{-1} = \boxed{-92.31 \text{ kJ mol}^{-1}}$$

$$\Delta_r H^\circ (H_2O(g)) = -483.64 \text{ kJ mol}^{-1} = \boxed{-241.82 \text{ kJ mol}^{-1}}$$

For an ideal gas  $\Delta H$  depends on change in temperature  $\therefore \Delta H = 0$

$\Delta V = 0$   
 $\Delta G = +1.58 \text{ kJ}$

$= (-1 \text{ mol}) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \left( \frac{0.7391 \text{ k}}{144.88} \right) = -1575 \text{ J} = -1.58 \text{ kJ}$

$W = - \int_{V_1}^{V_2} P \, dV = - \int_{V_1}^{V_2} \frac{nRT}{V} \, dV = -nRT \ln \left( \frac{V_2}{V_1} \right)$

$= 273.91 \text{ K}$

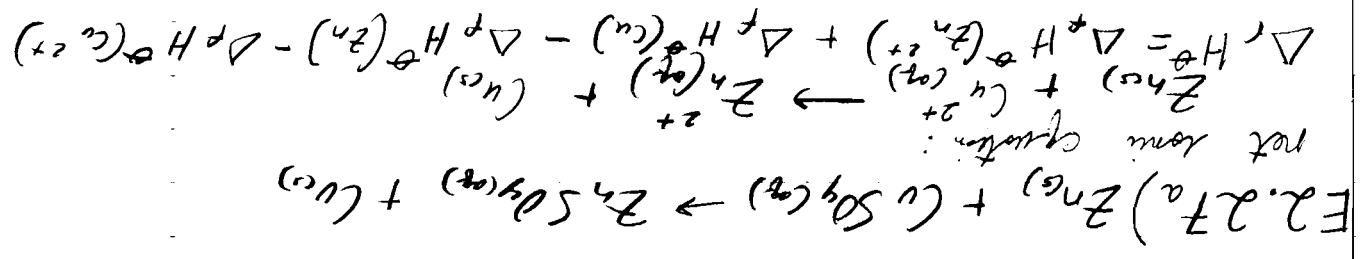
3:  $P = 0.50 \text{ atm}$ ,  $V = 49.88 \text{ dm}^3$   
 $T = \frac{(0.50 \text{ atm}) (49.88 \text{ dm}^3)}{(1 \text{ mol}) (8.206 \times 10^{-5} \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})} = 273.91 \text{ K}$

$= 596.92 \text{ K}$

2:  $P = 1.0 \text{ atm}$ ,  $V = 49.88 \text{ dm}^3$   
 $T = \frac{(1.0 \text{ atm}) (49.88 \text{ dm}^3)}{(1 \text{ mol}) (8.206 \times 10^{-5} \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})} = 596.92 \text{ K}$

2.1)  $PV = nRT$ ,  $P = 1.0 \text{ atm}$ ,  $V = 22.44 \text{ dm}^3$   
 $T = \frac{PV}{nR} = \frac{(1.0 \text{ atm}) (22.44 \text{ dm}^3)}{(1 \text{ mol}) (8.206 \times 10^{-5} \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})} = 273.91 \text{ K}$

$= [-153.89 + 0 + 0 - 64.77] \text{ kJ mol}^{-1} = -218.66 \text{ kJ mol}^{-1}$



$$\Delta H_2 = 0$$

$$\Delta H_2 = 3.91 \text{ kJ} + nR\Delta T = 3.91 \text{ kJ} - 2.27 \text{ kJ} = 1.64 \text{ kJ}$$

$$\Delta H_1 = -3.91 \text{ kJ} + nR\Delta T = -3.91 \text{ kJ} + 2.27 \text{ kJ} = -1.64 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta PV$$

$$q_1 = -3.91 \text{ kJ} - 2.27 \text{ kJ} = -568 \text{ kJ}$$

$$q_1 = \Delta U_1 - w_1; w_1 = p\Delta V = (101325 \text{ N/m}^2)(0.02199 \text{ m}^3) = 2213.7 \text{ J} = 2.21 \text{ kJ}$$

$$q_1 = \Delta U_1 - 2.21 \text{ kJ} = -568 \text{ kJ} \Rightarrow \Delta U_1 = -570.21 \text{ kJ}$$

$$q_2 = C_V \Delta T = 3.91 \text{ kJ}$$

$$\Delta U_1 = -\Delta U_2 = -3.91 \text{ kJ}$$

$$\Delta U_2 = C_V \Delta T = \frac{5}{2} R (1 \text{ mol}) (23.16 \text{ K}) = 3910 \text{ J} = 3.91 \text{ kJ}$$

$$w_1 + q_1 = -q_2$$

$$w_1 + C_V \Delta T = -C_V \Delta T$$

$$\Delta U_1 = q_1 + w_1 = q_2 - w_2 = -\Delta U_2$$

$$\Delta U_1 = -\Delta U_2$$

$$\Delta U_{\text{total}} = 0 \text{ for cyclic process}$$

$$\Delta U_3 = 0 \text{ for isotherm}$$

$$\Delta U_{\text{total}} = \Delta U_1 + \Delta U_2 + \Delta U_3 = 0$$

