

1) A sample consisting of 1.00 mol of the molecules in air is expanded isothermally at 25° C from 24.2 dm<sup>3</sup> to 48.4 dm<sup>3</sup> (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

For all cases  $\Delta U = 0$ , since the internal energy of a perfect gas depends only on temperature. (See *Molecular interpretation* 2.2 and Section 2.11(b) for a more complete discussion.) From the definition of enthalpy,  $H = U + pV$ , so  $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$  (perfect gas). Hence,  $\Delta H = 0$  as well, at constant temperature for all processes in a perfect gas.

(a)  $\Delta U = \Delta H = 0$

$$w = -nRT \ln \left( \frac{V_f}{V_i} \right) \quad [2.11]$$

$$= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left( \frac{48.4 \text{ dm}^3}{24.2 \text{ dm}^3} \right)$$

$$= -1.72 \times 10^3 \text{ J} = \boxed{-1.72 \text{ kJ}}$$

$$q = \Delta U - w \text{ [First Law]} = 0 + 1.72 \text{ kJ} = \boxed{+1.72 \text{ kJ}}$$

(b)  $\Delta U = \Delta H = 0$

$$w = -p_{\text{ex}} \Delta V \quad [2.8] \quad \Delta V = (48.4 - 24.2) \text{ dm}^3 = 24.2 \text{ dm}^3$$

$p_{\text{ex}}$  can be computed from the perfect gas law

$$pV = nRT$$

$$\text{so } p_{\text{ex}} = p_f = \frac{nRT}{V_f} = \frac{(1.00 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{48.4 \text{ dm}^3} = 0.505 \text{ atm}$$

$$w = -(0.505 \text{ atm}) \times \left( \frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \times (24.2 \text{ dm}^3) \times \left( \frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \right)$$

$$= -1.24 \times 10^3 \text{ Pa m}^3 = -1.24 \times 10^3 \text{ J} = \boxed{-1.24 \text{ kJ}}$$

$$q = \Delta U - w = 0 + 1.24 \text{ kJ} = \boxed{+1.24 \text{ kJ}}$$

(c)  $\Delta U = \Delta H = 0$

Free expansion is expansion against no force, so  $w = 0$  and  $q = \Delta U - w = 0 - 0 = \boxed{0}$

**Comment:** An isothermal free expansion of a perfect gas is also adiabatic.

2) A sample of oxygen of mass 96 g at 25.0 °C is allowed to expand reversibly and adiabatically from 5.00 dm<sup>3</sup> to 10.00 dm<sup>3</sup>. What is the work done by the gas?

Reversible adiabatic work is

$$w = C_V \Delta T \quad [2.27] = n(C_{p,m} - R) \times (T_f - T_i)$$

where the temperatures are related by

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{1/c} \quad [2.28a] \quad \text{where} \quad c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = 2.531$$

$$\text{So } T_f = [(25.0 + 273.15) \text{ K}] \times \left( \frac{5.00 \text{ dm}^3}{10.00 \text{ dm}^3} \right)^{1/2.531} = 227 \text{ K}$$

$$\text{and } w = \left( \frac{96.0 \text{ g}}{32.0 \text{ g mol}^{-1}} \right) \times [(29.355 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}] \times (227 - 298) \text{ K} = \boxed{-4.48 \text{ kJ}}$$

3) When 5.00 mol  $N_2$  is heated at a constant pressure of 3.00 atm, its temperature increases from 298 K to 345 K. Given that the molar heat capacity of  $N_2$  at constant pressure is  $29.125 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate  $q$ ,  $\Delta H$ , and  $\Delta U$ .

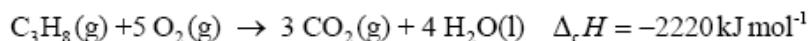
$$q_p = C_p \Delta T [2.24] = nC_{p,m} \Delta T = (5.00 \text{ mol}) \times (29.1 \text{ J K}^{-1} \text{ mol}^{-1}) \times (47 \text{ K}) = \boxed{+6.8 \text{ kJ}}$$

$$\Delta H = q_p [2.23b] = \boxed{+6.8 \text{ kJ}}$$

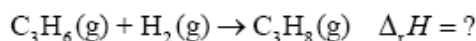
$$\begin{aligned} \Delta U &= \Delta H - \Delta(pV) [\text{From } H \equiv U + pV] = \Delta H - \Delta(nRT) [\text{perfect gas}] = \Delta H - nR\Delta T \\ &= (6.8 \text{ kJ}) - (5.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (47 \text{ K}) = (6.8 \text{ kJ}) - (1.95 \text{ kJ}) = \boxed{+4.8 \text{ kJ}} \end{aligned}$$

4) The standard enthalpy of combustion of n-propane ( $C_3H_8$ ) is  $-2220 \text{ kJ mol}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . From this information and enthalpy of formation data for  $CO_2(g)$  and  $H_2O(g)$ , calculate the enthalpy of formation of n-propane. The enthalpy of formation of propene ( $C_3H_6$ ) is  $+20.42 \text{ kJ mol}^{-1}$ . Calculate the enthalpy of hydrogenation of propene to propane.

First  $\Delta_f H[C_3H_8, g]$  is calculated, and then that result is used to calculate  $\Delta_f H$  for the hydrogenation



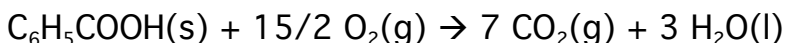
$$\begin{aligned} \Delta_f H[C_3H_8, g] &= -\Delta_c H + 3\Delta_f H(CO_2, g) + 4\Delta_f H(H_2O, g) \\ &= [+2220 + (3) \times (-393.51) + (4) \times (-285.83)] \text{ kJ mol}^{-1} \\ &= \boxed{-103.85 \text{ kJ mol}^{-1}} \end{aligned}$$



$$\begin{aligned} \Delta_f H &= \Delta_f H(C_3H_8, g) - \Delta_f H[C_3H_6, g] \\ &= (-103.85 - 20.42) \text{ kJ mol}^{-1} = \boxed{-124.27 \text{ kJ mol}^{-1}} \end{aligned}$$

5) Benzoic Acid ( $C_6H_5COOH$ ) is a commonly used standard used for determining the calorimeter constant of a bomb calorimeter. The enthalpy of combustion for benzoic acid is very well known and is found to be  $\Delta_c H^\circ = -3227 \text{ kJ/mol}$ . If a  $0.596 \text{ g}$  of benzoic acid is combusted in a bomb calorimeter and found to produce a  $0.95 \text{ }^\circ\text{C}$  rise in temperature, calculate the calorimeter constant for the apparatus.

If  $0.568 \text{ g}$  of naphthalene ( $C_{10}H_8$ ) is subsequently combusted in the bomb calorimeter at the same conditions, and produces a  $1.56 \text{ }^\circ\text{C}$  rise in temperature, calculate the enthalpy of combustion of naphthalene.



$$\Delta H_m = \Delta U_m + \Delta nRT$$

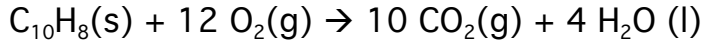
$$-3227 \text{ kJ/mol} = \Delta U_m + ((7 - 15/2) \times 8.314 \times 298)$$

$$\Delta U_m = -3225.7 \text{ kJ/mol}$$

$$\Delta U = -3225.7 \text{ kJ/mol} \times (0.596 \text{ g} / 122 \text{ g/mol}) = -15.76 \text{ kJ}$$

$$|q_v| = |\Delta U| = 15.76 \text{ kJ}$$

$$C = q_v / \Delta T = 15.76 \text{ kJ} / 0.95 \text{ K} = 16.59 \text{ kJ} / \text{K}$$



$$q_v = C \Delta T = 16.59 \text{ kJ / K} \times 1.56 \text{ K} = 25.88 \text{ kJ} = \Delta U$$

$$\Delta U = 25.88 \text{ kJ} / (0.568 \text{ g} / 128 \text{ g mol}^{-1}) = -5829 \text{ kJ/mol}$$

$$\begin{aligned} \Delta H_m &= \Delta U_m + \Delta nRT = -5829 \text{ kJ/mol} + ((10-12) \times 8.314 \times 298) \\ &= -5834 \text{ kJ/mol} \end{aligned}$$

6) A sample of nitrogen gas is adiabatically expanded such that its volume triples. If the sample initially is held 25 °C, what is the final temperature of the gas? Given that the initial pressure is 1 atm and the volume is 500 mL, calculate the work done.

$$w = C_v \Delta T = n(C_{p,m} - R) \times (T_f - T_i)$$

$$T_f = T_i (V_i / V_f)^{1/c} \quad \text{where } c = (C_{v,m}) / R = (C_{p,m} - R) / R = 2.503$$

$$\text{So } T_f = 298 \text{ K} (1/3)^{1/2.503} = 189 \text{ K}$$

$$\text{So if } w = n(C_{p,m} - R) \times (T_f - T_i) = (PV / RT) \times (29.125 - 8.314) \times (189 - 298)$$

$$= (1 \text{ atm} \times 0.5 \text{ L}) / (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) (20.811) (-109)$$

$$= -46 \text{ J}$$