

1. The volumetric thermal expansion coefficient  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$  gives the fractional change in  
[1] the volume of a system heated at constant pressure. For an ideal gas, prove  $\beta = 1/T$ .

2. a) Prove the differential  $df$  defined by  $df = dx - \frac{x}{y} dy$  is inexact, and therefore the function  $f(x,y)$  does not exist.

- [2] b) Prove the differential  $dg$  defined by  $dg = \frac{1}{y} dx$  is exact, and therefore the function  $g(x,y)$  exists. For a bonus point, give  $g(x,y)$ .

3. a) An ideal gas ( $p = RT/V_m$ ) is compressed reversibly ( $p_{\text{external}} = \text{gas pressure } p$ ) and isothermally (constant temperature) from initial molar volume  $V_{mi}$  to final molar volume  $V_{mf}$ . Show

$$w = -nRT \ln \left( \frac{V_{mf}}{V_{mi}} \right)$$

- [3] b) A gas with attractive intermolecular forces obeying the equation of state

$$p = \frac{RT}{V_m} - \frac{a}{V_m^2}$$

is reversibly and isothermally compressed from  $V_{mi}$  to  $V_{mf}$ . For this nonideal gas, show

$$w = -nRT \ln \left( \frac{V_{mf}}{V_{mi}} \right) - na \left( \frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right)$$

- c) Use the results from **a** and **b** to show that attractive intermolecular forces reduce the amount of work required to compress a gas.

4. Explain briefly, in molecular terms, why

a)  $C_{V,m}$  for He(g) is  $3R/2$ .

- [3] b)  $C_{V,m}$  for O<sub>2</sub>(g) is larger than  $C_{V,m}$  for He(g)

c)  $C_{V,m}$  for O<sub>2</sub>(g) increases with temperature.

... page 2

5. 5.00 moles of He (assumed to be an ideal gas) initially at 300 K and 1.00 bar is compressed isothermally to a final pressure of 4.00 bar.
- a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  if the compression is performed reversibly.
- [4] b) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  if the compression is performed irreversibly with a constant 4.00 bar external pressure.
6. Question 3 shows that  $U$  and  $H$  are state functions but  $q$  and  $w$  are path-dependent. Explain. [1]
7. 500 grams of liquid water initially at 20 °C is heated to 100 °C at 1.00 bar in an electric kettle.
- a)  $w$  is negligibly small ( $\approx$  zero) for this process. Why?
- b) Calculate  $q$ ,  $\Delta U$  and  $\Delta H$ .
- [4] c) **Nova Scotia Power** charges residential customers \$0.174 per kilowatt hour of electrical energy. Estimate the cost of the electricity required to heat the water from 20 °C to 100 °C.
- d) The actual cost of electricity required to heat the water in the kettle is significantly larger than the value calculated in c. Why?
- Data:  $C_{pm}(\text{H}_2\text{O},l) = 75.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $MW(\text{H}_2\text{O}) = 18.0 \text{ g mol}^{-1}$
8. Suppose the hull of the International Space Station is holed by a meteorite impact, causing the air onboard to expand rapidly and adiabatically into the vacuum of space. For this gas expansion process:  $q = w = \Delta U = \Delta H = 0$ . Explain! [2]

(Q1) For an ideal  $V = \frac{nRT}{P}$  and

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$= \frac{1}{\frac{nRT}{P}} \left( \frac{\partial \frac{nRT}{P}}{\partial T} \right)_P = \frac{P}{nRT} \frac{nR}{P} \left( \frac{\partial T}{\partial T} \right)_P$$

$$= \frac{1}{T}$$

(Q2) a)  $df = (1) dx + \left(-\frac{x}{y}\right) dy$

$df$  is exact ~~if~~  $\left( \frac{\partial 1}{\partial y} \right)_x = \left( \frac{\partial -\frac{x}{y}}{\partial x} \right)_y$

$$LS = \left( \frac{\partial 1}{\partial y} \right)_x = 0$$

$$RS = \left( \frac{\partial \left(-\frac{x}{y}\right)}{\partial x} \right)_y = -\frac{1}{y} \left( \frac{\partial x}{\partial x} \right)_y = -\frac{1}{y}$$

$$LS \neq RS$$

$df$  is inexact

$f(x,y)$  does not exist

(Q2 cont.)

$$b) \quad dg = \frac{1}{y} dx = \frac{dx - \frac{x}{y} dy}{y}$$

$$dg = \frac{1}{y} dx - \frac{x}{y^2} dy$$

dg is exact ~~if~~  $\left(\frac{\partial \frac{1}{y}}{\partial y}\right)_x = \left(\frac{\partial -\frac{x}{y^2}}{\partial x}\right)_y$

$$LS = \left(\frac{\partial \frac{1}{y}}{\partial y}\right)_x$$

$$= -\frac{1}{y^2}$$

$$RS = -\frac{1}{y^2} \left(\frac{\partial x}{\partial x}\right)_y$$

$$= -\frac{1}{y^2}$$

$$LS = RS$$

this means the function  $g(x, y)$  exists

for example,  $g(x, y) = c_1 \frac{x}{y} + c_2$  ( $c_1, c_2$  are constants)

Q3 a)  $n$  moles of an ideal gas are compressed reversibly and isothermally from  $V_{mi}$  to  $V_{mf}$  ( $P_{ext} = P$ )

$$w = - \int P_{ext} dV = - \int P dV = - \int P dV = - \int \frac{nRT}{V} dV$$

$$= -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -nRT (\ln V) \Big|_{V_i}^{V_f}$$

$$= -nRT (\ln V_f - \ln V_i) = -nRT \ln \left(\frac{V_f}{V_i}\right) = -nRT \ln \left(\frac{V_{mf}}{V_{mi}}\right)$$

(Q3 cont.)

b)  $n$  moles of a nonideal gas with attractive intermolecular forces are reversibly and isothermally compressed ( $V_f < V_i$ ):  
( $P_{ext} = P$ )

$$w = - \int P_{ext} dV = - \int p dV$$

$$V = n V_m \quad \text{constant}$$
$$dV = n dV_m$$

$$= - \int \left( \frac{RT}{V_m} - \frac{a}{V_m^2} \right) dV$$

$$= - n \int_{V_{mi}}^{V_{mf}} \left( \frac{RT}{V_m} - \frac{a}{V_m^2} \right) dV_m = - nRT \int_{V_{mi}}^{V_{mf}} \frac{1}{V_m} dV_m + na \int_{V_{mi}}^{V_{mf}} \frac{1}{V_m^2} dV_m$$

$$= - nRT (\ln V_m) \Big|_{V_{mi}}^{V_{mf}} + na \left( -\frac{1}{V_m} \right) \Big|_{V_{mi}}^{V_{mf}}$$

$$= - nRT (\ln V_{mf} - \ln V_{mi}) + na \left[ -\frac{1}{V_{mf}} - \left( -\frac{1}{V_{mi}} \right) \right]$$

$$w = - nRT \ln \left( \frac{V_{mf}}{V_{mi}} \right) - na \left( \frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right)$$

c) The work  $w$  required to compress ( $V_f < V_i$ ) a gas is positive (work is done on the gas).

For a compression,  $\frac{1}{V_{mf}}$  is greater than  $\frac{1}{V_{mi}}$

so the work term  $-na \left( \frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right)$  is negative (from attractive forces)

reducing the magnitude of  $w$  (positive overall)

Q4

a) He is a monatomic gas (no molecular vibrations or rotations).

At ambient temperatures (no high-energy excited electronic states) the energy of He is translational kinetic energy for motion in the  $x$ ,  $y$  and  $z$  directions,  $\frac{1}{2}RT$  molar energy for each of the three "degrees of freedom."

$$U_m = \frac{1}{2}RT + \frac{1}{2}RT + \frac{1}{2}RT = \frac{3}{2}RT$$

$$C_{vm} = \left( \frac{\partial U_m}{\partial T} \right)_v = \left( \frac{\partial}{\partial T} \frac{3}{2}RT \right)_v = \frac{3}{2}R$$

b)  $C_{vm}(O_2, g) > C_{vm}(He, g)$  because  $O_2$  has rotational and vibrational energy that He does not have, so  $U_m(O_2, g) > U_m(He, g)$  at a given temperature

c)  $C_{vm}(O_2, g)$  increases with temperature because vibration of the  $O=O$  bond becomes more active, absorbing more energy as  $O_2$  is heated

Q5) 5.00 moles of He(g) at 300 K, 1.00 bar compressed isothermally ( $T=300\text{ K}$ ) to 4.00 bar

a) reversible compression ( $p_{\text{ext}} = p = \frac{nRT}{V}$ )

$$w = - \int p_{\text{ext}} dV = - \int p dV = - \int \frac{nRT}{V} dV$$

$$= -nRT \int \frac{1}{V} dV = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$= -nRT \ln\left(\frac{\frac{nRT}{p_f}}{\frac{nRT}{p_i}}\right) = -nRT \ln\left(\frac{p_i}{p_f}\right) = nRT \ln\left(\frac{p_f}{p_i}\right)$$

$$= (5.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln\left(\frac{4.00 \text{ bar}}{1.00 \text{ bar}}\right)$$

$$w = 17,300 \text{ J}$$

for an isothermal gas  $(\partial U / \partial V)_T = 0$ , so the energy is fixed

$$\Delta U = 0$$

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

so

$$q = -w$$
$$q = -17,300 \text{ J}$$

$$\Delta H = \Delta(U + pV) = \Delta U + \Delta(pV)$$

$$= \Delta U + \Delta(nRT)$$

$$= \overset{0}{\Delta U} + nR \overset{0}{\Delta T}$$

$$= 0 + 0$$

$$\Delta H = 0$$

(Q5 cont.)

b) irreversible compression at 300 K,  $P_{\text{ext}} = 4.00 \text{ bar}$  (constant)  
 $P_{\text{ext}} (= P_f)$

$$w = - \int P_{\text{ext}} dV = - P_{\text{ext}} \int dV = - P_{\text{ext}} (V_f - V_i)$$

$$w = - P_{\text{ext}} \left( \frac{nRT}{P_f} - \frac{nRT}{P_i} \right) = - nRT \left( \frac{P_{\text{ext}}}{P_f} - \frac{P_{\text{ext}}}{P_i} \right)$$

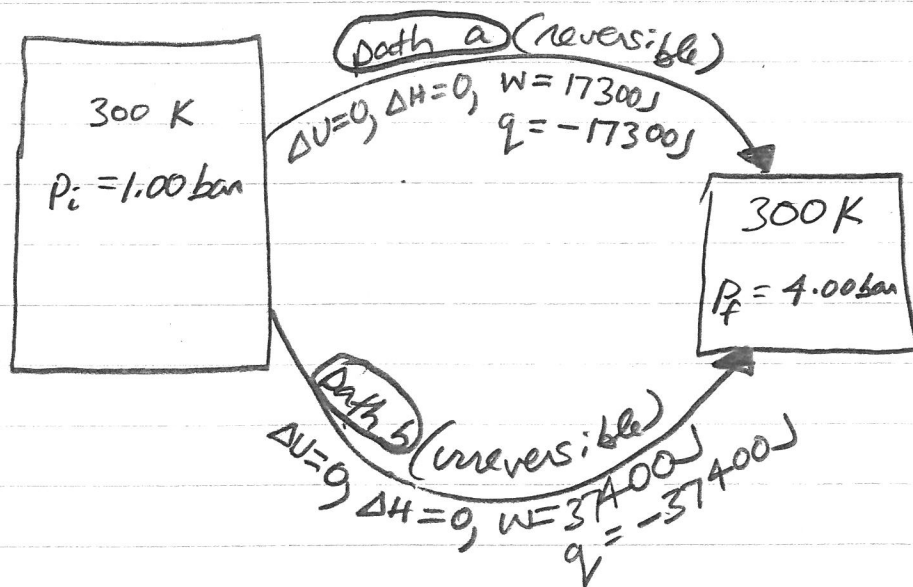
$$w = - (5.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) 300 \text{ K} \left( \frac{4.00 \text{ bar}}{4.00 \text{ bar}} - \frac{4.00 \text{ bar}}{1.00 \text{ bar}} \right)$$

$$w = 37400 \text{ J}$$

isothermal ideal gas:  $\Delta U = 0$   
 $\Delta H = 0$

$$q = -w = -37400 \text{ J}$$

Q6



$\Delta U, \Delta H$  are path-independent (state functions)

$q, w$  are path-dependent (not state functions)



Q7

500 g ( $n = 27.8 \text{ mol}$ ) liquid water  
is heated from  $20^\circ\text{C}$  to  $100^\circ\text{C}$  at 1.00 bar

$293.15 \text{ K}$

$373.15 \text{ K}$

$$a) \quad w = -\int P_{\text{ext}} dV = -P \int dV = -P \Delta V$$

the volume  $V$  of liquid water is very small  
(about 0.018 L per mole) compared to the  
volume of gases (about 25 L per mole at  $20^\circ\text{C}$ , 1 bar).

The change in volume ( $\Delta V$ ) produced by heating  
liquid water is even smaller, so  $w = -P \Delta V \approx 0$ .

$$b) \quad C_p = \frac{dq_p}{dT} \Rightarrow dq_p = C_p dT = n C_{p,m} dT$$

$$q_p = \int C_p dT = \int n C_{p,m} dT = n C_{p,m} \int dT = n C_{p,m} \Delta T$$

$$q_p = (27.8 \text{ mol})(75.6 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 - 293.15) \text{ K}$$

$$q_p = 168,000 \text{ J} \quad \Delta U = q_p + w_p^0 = 168,000 \text{ J}$$

$$\Delta H = q_p = 168,000 \text{ (constant pressure)}$$

$$c) \quad \text{cost of electrical energy} = \frac{\$0.174}{\text{kWh}} \frac{1}{1000 \text{ J s}^{-1}} \frac{1}{3600 \frac{\text{s}}{\text{h}}} \\ = 4.80 \times 10^{-8} \text{ \$/J}$$

(Q7 c conti.)

cost of 168,000 J of electrical energy

$$= (168,000 \text{ J}) (4.80 \times 10^{-8} \text{ \$ J}^{-1})$$

$$= 0.00806 \text{ \$} \quad = 0.806 \text{ ¢}$$

d) The actual cost to heat the water is larger because some of the electrically-supplied heat is lost to the surrounding air and kettle, and does not contribute to heating the water. Also, some of the water evaporates, requiring more heat.

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(Q8) adiabatic expansion into a vacuum ( $P_{\text{ext}} = 0$ )

$$q = 0 \quad (\text{adiabatic process})$$

$$w = - \int P_{\text{ext}} dV = - \int (0) dV = 0$$

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

U depends only on T for an ideal gas

if  $\Delta U = 0$ , then  $\Delta T = 0$  and

$$\begin{aligned} \Delta H &= \Delta(U + pV) = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) \\ &= \Delta U + nR\Delta T \\ &= 0 + 0 \\ &= 0 \end{aligned}$$