

## Chapter 4

1. Given the relationship

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

show that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

for an ideal gas.

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Plugging this into the expression

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

Yields

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{nR}{V}\right) - p$$

And noting that

$$T \left(\frac{nR}{V}\right) = p$$

It can be seen that

$$\left(\frac{\partial U}{\partial V}\right)_T = p - p = 0$$

2. Determine if the following differential is exact, and if so, find the function  $z(x, y)$  that satisfies the expression.

$$dz = 4xy \, dx + 2x^2 \, dy$$

In order to be an exact differential, the following must hold:

$$\frac{\partial}{\partial y} P(x, y) = \frac{\partial}{\partial x} Q(x, y)$$

where

$$P(x, y) = 4xy \quad \text{and} \quad Q(x, y) = 2x^2$$

So,

$$\frac{\partial}{\partial y} (4xy) = 4x$$

And

$$\frac{\partial}{\partial x} (2x^2) = 4x$$

So, in fact

$$\frac{\partial}{\partial y} P(x, y) = \frac{\partial}{\partial x} Q(x, y)$$

So the differential is exact.

To find the original function  $z(x, y)$  we need to note that

$$\left( \frac{\partial z}{\partial x} \right)_y = 4xy \quad \text{and} \quad \left( \frac{\partial z}{\partial y} \right)_x = 2x^2$$

From the first expression, integration yields

$$z = y \int 4x \, dx = 2x^2 y + \text{const.}$$

The second expression yields something similar.

$$z = 2x^2 \int dy = 2x^2 y + \text{const.}$$

So the function is

$$z(x, y) = 2x^2y + \text{const.}$$

3. For a van der Waals gas,  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ . Find an expression in terms of  $a$ ,  $n$ ,  $V$ , and  $R$  for  $\left(\frac{\partial T}{\partial V}\right)_U$  if  $C_V = 3/2 R$ . Use the expression to calculate the temperature change for 1.00 mol of Xe ( $a = 4.19 \text{ atm L}^2 \text{ mol}^{-2}$ ) expanding at constant internal energy against a vacuum from 10.0 L to 20.0 L.

Consider  $U(V, T)$ . This allows one to write the expression for the total differential

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Now, dividing by  $dV$  and constraining to constant  $U$  generates

$$\left.\frac{dU}{dV}\right|_U = \left(\frac{\partial U}{\partial V}\right)_T \left.\frac{dV}{dV}\right|_U + \left(\frac{\partial U}{\partial T}\right)_V \left.\frac{dT}{dV}\right|_U$$

Which simplifies to

$$0 = \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

And solving for  $\left(\frac{\partial T}{\partial V}\right)_U$  and substituting for  $\left(\frac{\partial U}{\partial V}\right)_T$  for a van der Waals gas (and keeping in mind that the heat capacity for the system depends on the amount of substance undergoing the expansion)

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = -\frac{1}{nC_V} \frac{an^2}{V^2} = -\frac{an}{C_V V^2}$$

In order to get the temperature change for a constant internal energy expansion, we need to evaluate

$$\Delta T = \int_{V_1}^{V_2} \left(\frac{\partial T}{\partial V}\right)_U dV$$

So, substituting from above,

$$\Delta T = -\frac{an}{C_V} \int_{V_1}^{V_2} \frac{dV}{V^2} = \frac{an}{C_V} \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

So

$$\Delta T = \frac{(4.19 \text{ atm L}^2 \text{ mol}^{-2})(1.00 \text{ mol})}{\left(\frac{3}{2} \cdot 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}\right)} \left( \frac{1}{20.0 \text{ L}} - \frac{1}{10.0 \text{ L}} \right) = -1.70 \text{ K}$$

Note the choice of the units on R in order to cancel the units given in the constant  $a$ !

4. Given the following data, calculate the change in volume for 50.0 cm<sup>3</sup> of a) neon and b) copper due to a decrease in pressure from 1.00 atm to 0.750 atm at 298 K.

Substance	$\kappa_T$ (at 1.00 atm and 298 K)
<b>Ne</b>	1.00 atm <sup>-1</sup>
<b>Cu</b>	0.735 x 10 <sup>-6</sup> atm <sup>-1</sup>

To solve this problem, we need an expression for the isothermal compressibility coefficient for these substances.

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

The change in volume is then given by

$$\Delta V = \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial p} \right)_T dp = - \int_{p_1}^{p_2} V \kappa_T dp$$

If the change in volume is very small (as will be the case for solid copper), we can approximate  $V$  as  $V_i$ . and if  $\kappa_T$  is constant over the pressure range, the expression becomes

$$\Delta V = -V_i \kappa_T \Delta p$$

So for Cu,

$$\begin{aligned} \Delta V &= -(50.0 \text{ cm}^3)(0.735 \cdot 10^{-6} \text{ atm}^{-1})(0.750 \text{ atm} - 1.00 \text{ atm}) \\ &= 9.2 \cdot 10^{-6} \text{ cm}^3 \end{aligned}$$

For a gas, such as neon, the volume will be highly dependent on the pressure. If we assume the gas is ideal,

$$V = \frac{nRT}{p}$$

And the expression for  $\Delta V$ , which is to be derived from

$$\Delta V = \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial p} \right)_T dp$$

The derivative can be determined analytically.

$$\left( \frac{\partial V}{\partial p} \right)_T = -\frac{nRT}{p^2}$$

So

$$\begin{aligned} \Delta V &= -nRT \int_{p_1}^{p_2} \frac{dp}{p^2} \\ &= nRT \left[ \frac{1}{p} \right]_{p_1}^{p_2} \\ &= nRT \left( \frac{1}{p_2} - \frac{1}{p_1} \right) \end{aligned}$$

We can find an expression for  $n$  using the initial pressure, volume, and temperature.

$$n = \frac{p_1 V_1}{RT}$$

So,

$$\begin{aligned} \Delta V &= \left( \frac{p_1 V_1}{RT} \right) RT \left[ \frac{1}{p_1} - \frac{1}{p_2} \right] = p_1 V_1 \left( \frac{1}{p_2} - \frac{1}{p_1} \right) \\ &= (1.00 \text{ atm})(50.0 \text{ cm}^3) \left( \frac{1}{0.750 \text{ atm}} - \frac{1}{1.00 \text{ atm}} \right) \\ &= 16.7 \text{ cm}^3 \end{aligned}$$

Notice that if we had used Boyle's Law

$$\begin{aligned} p_1 V_1 &= p_2 V_2 \\ (1.00 \text{ atm})(50.0 \text{ cm}^3) &= (0.750 \text{ atm})(V_2) \end{aligned}$$

$$V_2 = 66.7 \text{ cm}^3$$

And

$$\Delta V = V_2 - V_1 = 66.7 \text{ cm}^3 - 50.0 \text{ cm}^3 = 16.7 \text{ cm}^3$$

We would have gotten the identical result!

5. Consider a gas that follows the equation of state

$$p = \frac{nRT}{V - nb}$$

derive an expression for

a. the isobaric thermal expansivity,  $\alpha$

The isobaric thermal expansivity is defined by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

This can be easily evaluated by solving the equation of state for V:

$$V = \frac{nRT}{p} + nb$$

Differentiating this with respect to T at constant p yields

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$$

And so, the expression for  $\alpha$  is given by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{pV}$$

b. the Joule-Thomson coefficient,  $\mu_{JT}$

$$\mu_{JT} = \frac{V}{C_p} (T\alpha - 1)$$

From the previous result,

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$$

So, because  $\mu_{JT} = \frac{1}{c_p} (TV\alpha - V)$ , it follows

$$\mu_{JT} = \frac{1}{c_p} \left( TV \left[ \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \right] - V \right)$$

$$\mu_{JT} = \frac{1}{c_p} \left[ T \left( \frac{nR}{p} \right) - V \right]$$

According to this particular equation of state,

$$\frac{nRT}{p} = V - nb$$

So

$$\mu_{JT} = \frac{1}{c_p} \left[ \frac{nRT}{p} - V \right] = \frac{1}{c_p} (V - nb - V) = -\frac{nb}{c_p}$$

6. Given

$$\left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V$$

derive an expression for  $\left(\frac{\partial U}{\partial p}\right)_T$  in terms of measurable properties. Use your result to calculate the change in the internal energy of 18.0 g of water when the pressure is increased from 1.00 atm to 20.0 atm at 298 K.

Starting from the definition of enthalpy

$$H = U + pV$$

Differentiating produces

$$dH = dU + p dV + V dp$$

Now, dividing by dp and constraining to constant T,

$$\left. \frac{dH}{dp} \right|_T = \left. \frac{dU}{dp} \right|_T + p \left. \frac{dV}{dp} \right|_T + V \left. \frac{dp}{dp} \right|_T$$

which simplifies to

$$\left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial U}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T + V$$

Substituting the relationship given in the problem

$$-T \left( \frac{\partial V}{\partial T} \right)_p + V = \left( \frac{\partial U}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T + V$$

The volume terms cancel. Upon substitution using the definitions of  $\alpha$  and  $\kappa_T$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

the expression becomes

$$-TV\alpha = \left( \frac{\partial U}{\partial p} \right)_T - pV\kappa_T$$

or

$$\left( \frac{\partial U}{\partial p} \right)_T = TV\alpha - pV\kappa_T$$

For the rest of this, we need to look up values of  $\alpha$  and  $\kappa_T$  for water and solve the integral

$$\Delta U = \int_{1.00 \text{ atm}}^{20.0 \text{ atm}} (TV\alpha - pV\kappa_T) dp$$

7. Derive an expression for  $\left( \frac{\partial U}{\partial T} \right)_p$ . Begin with the definition of enthalpy, in order to determine

$$dH = dU + pdV + Vdp$$

Finish by dividing by dT and constraining to constant pressure. Make substitutions for the measurable quantities, and solve for  $\left( \frac{\partial U}{\partial T} \right)_p$ .



$$\left. \frac{dH}{dT} \right|_p = \left. \frac{dU}{dT} \right|_p + p \left. \frac{dV}{dT} \right|_p + V \left. \frac{dp}{dT} \right|_p$$

The last term of this vanishes (due to  $dp = 0$ ), so after some substitution, the expression becomes

$$C_p = \left( \frac{\partial U}{\partial T} \right)_p + pV\alpha$$

Or

$$\left( \frac{\partial U}{\partial T} \right)_p = C_p - pV\alpha$$

8. Derive an expression for the difference between  $C_p$  and  $C_v$  in terms of the internal pressure,  $\alpha$ ,  $p$  and  $V$ . Using the definition for  $H$  as a starting point, show that

$$\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p$$

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

Now divide by  $dT$  and constrain to constant  $p$ :

$$\left. \frac{dH}{dT} \right|_p = \left. \frac{dU}{dT} \right|_p + p \left. \frac{dV}{dT} \right|_p + V \left. \frac{dp}{dT} \right|_p$$

The last term vanished (since  $dp = 0$  at constant  $p$ ) so the expression becomes

$$\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p$$

Now, find an expression for  $\left( \frac{\partial U}{\partial T} \right)_p$  by starting with  $U(V,T)$  and writing an expression for the total differential  $dU$ .

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT$$

Divide by  $dp$  and constrain to constant  $T$ . Substitute this into the previous expressions and solve for  $\left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V$ .

From the total differential, divide by  $dT$  and constrain to constant  $p$ :

$$\left. \frac{dU}{dT} \right|_p = \left( \frac{\partial U}{\partial T} \right)_p \left. \frac{dV}{dT} \right|_p + \left( \frac{\partial U}{\partial T} \right)_V \left. \frac{dT}{dT} \right|_p$$

Which becomes

$$\left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + \left( \frac{\partial U}{\partial T} \right)_V$$

Plugging this into the expression for  $\left( \frac{\partial H}{\partial T} \right)_p$  yields

$$\left( \frac{\partial H}{\partial T} \right)_p = \left[ \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + \left( \frac{\partial U}{\partial T} \right)_V \right] + p \left( \frac{\partial V}{\partial T} \right)_p$$

Noting the following:

$$\left( \frac{\partial H}{\partial T} \right)_p = C_p; \left( \frac{\partial U}{\partial V} \right)_T = \pi_T; \left( \frac{\partial V}{\partial T} \right)_p = V\alpha; \text{ and } \left( \frac{\partial U}{\partial T} \right)_V = C_V$$

The expression becomes

$$C_p = \pi_T V \alpha + C_V + p V \alpha$$

Or

$$C_p - C_V = V(\pi_T \alpha + p \alpha)$$

9. Evaluate the expression you derived in problem 8 for an ideal gas, assuming that the internal pressure of an ideal gas is zero.

For an ideal gas,  $\pi_T = 0$  and  $\alpha = 1/T$ . So

$$C_p - C_V = \frac{pV}{T} = R$$