Chapter 4

1. Given the relationship

show that

for an ideal gas.

For an ideal gas,

So

Plugging this into the expression

Yields

And noting that

It can be seen that

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

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

where

and

So,

And

So, in fact

So the differential is exact.

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

and

From the first expression, integration yields

The second expression yields something similar.

So the function is

1. For a van der Waals gas, . Find an expression in terms of *a*, *n*, *V*, and *R* for if CV = 3/2 R. Use the expression to calculate the temperature change for 1.00 mol of Xe (*a* = 4.19 atm L2 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

Now, dividing by dV and constraining to constant U generates

Which simplifies to

And solving for and substituting for 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)

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

So, substituting from above,

So

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

1. Given the following data, calculate the change in volume for 50.0 cm3 of a) neon and b) copper due to a decrease in pressure from 1.00 atm to 0.750 atm at 298 K.

|  |  |
| --- | --- |
| Substance | T (at 1.00 atm and 298 K) |
| Ne | 1.00 atm-1 |
| Cu | 0.735 x 10-6 atm-1 |

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

The change in volume is then given by

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

So for Cu,

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

And the expression for DV, which is to be derived from

The derivative can be determined analytically.

So

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

So,

Notice that if we had used Boyle’s Law

And

We would have gotten the identical result!

1. Consider a gas that follows the equation of state

derive an expression for

1. the isobaric thermal expansivity, 

The isobaric thermal expansivity is defined by

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

Differentiating this with respect to T at constant p yields

And so, the expression for a is given by

1. the Joule-Thomson coefficient, JT

From the previous result,

So, because , it follows

An according to this particular equation of state,

So

1. Given

derive an expression for 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

Differentiating produces

Now, dividing by dp and constraining to constant T,

which simplifies to

Substituting the relationship given in the problem

The volume terms cancel. Upon substitution using the definitions of  and T

and

the expression becomes

or

For the rest of this, we need to look up values of  and T for water and solve the integral

1. Derive an expression for . Begin with the definition of enthalpy, in order to determine

Finish by dividing by dT and constraining to constant pressure. Make substitutions for the measurable quantities, and solve for .

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

Or

1. Derive an expression for the difference between Cp and CV in terms of the internal pressure, , p and V. Using the definition for H as a starting point, show that

Now divide by dT and constrain to constant p:

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

Now, find an expression for by starting with U(V,T) and writing an expression for the total differential dU.

Divide by dp and constrain to constant T. Substitute this into the previous expressions and solve for .

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

Which becomes

Plugging this into the expression for yields

Noting the following:

; ; ; and

The expression becomes

Or

1. 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, T  = 0 and  = 1/T. So