

Chapter 4: Putting the First Law to Work

As has been seen in previous chapters, many important thermochemical quantities can be expressed in terms of partial derivatives. Two important examples are the molar heat capacities C_p and C_v which can be expressed as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

These are properties that can be measured experimentally and tabulated for many substances. These quantities can be used to calculate changes in quantities since they represent the slope of a surface (H or U) in the direction of the specified path (constant p or V). This allows us to use the following kinds of relationships:

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT \quad \Delta H = \int \left(\frac{\partial H}{\partial T} \right)_p dT$$

Because thermodynamics is kind enough to deal in a number of state variables, the functions that define how those variables change must behave according to some very well determined mathematics. This is the true power of thermodynamics!

Total Differentials

The fact that we can define the constant volume heat capacity as $\left(\frac{\partial U}{\partial T} \right)_v$ suggests that the internal energy depends very intimately on two variables: volume and temperature. In fact, we will see that for a single component system, state variables are always determined when two state variables are defined. In the case of internal energy, we might write

$$U = f(V, T) \quad \text{or} \quad U(V, T)$$

This suggests that the way to change U is to change either V or T (or both!) And if there is a mathematical function that relates the internal energy to these two variables, it should be easy to see how it changes when either (or both!) are changed. This can be written as a **total differential**.

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

Even without knowing the actual mathematical function relating the variables to the property, we can imagine how to calculate changes in the property from this expression.

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V} \right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T} \right)_V dT$$

In words, this implies that we can think of a change in U occurring due to an isothermal change followed by an isochoric change. And all we need to know is the slope of the surface in each pathway direction.

There are a couple of very important experiments people have done to explore the measurement of those kinds of slopes. Understanding them, it turns out, depends on two very important physical properties of substances.

Exact Differentials

We have seen that the total differential of $U(V, T)$ can be expressed as

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

In general, if a differential can be expressed as

$$df(x, y) = Pdx + Qdy$$

the differential will be an **exact differential** if it follows the **Euler relation**

$$\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y$$

In order to illustrate this concept, consider $p(V, T)$ using the ideal gas law.

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

The total differential of p can be written

$$dp = \left(-\frac{RT}{V^2}\right)dV + \left(\frac{R}{V}\right)dT$$

Does this expression follow the Euler relation? Let's see!

$$\left[\frac{\partial}{\partial T}\left(-\frac{RT}{V^2}\right)\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{R}{V}\right)\right]_T$$

$$\left(-\frac{R}{V^2}\right) = \left(-\frac{R}{V^2}\right)$$

So it worked! dp is, in fact, an exact differential. This will be the case for all of the thermodynamic functions that are state functions.

Isothermal Compressibility (κ_T)

A very important property of a substance is how compressible it is. Gases are very compressible, so when subjected to high pressures, their volumes decrease significantly (think Boyle's Law!) Solids and liquids however are not as compressible. However, they are not entirely incompressible! High pressure will lead to a decrease in volume, even if it is only slight. And, of course, different substances are more compressible than others.

In order to quantify just how compressible substances are, it is necessary to define the property. The **isothermal compressibility** is defined by the fractional differential change in volume due to a change in pressure.

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

The negative sign is important in order to keep the value of κ_T positive, since an increase in pressure will lead to a decrease in volume. The $1/V$ term is needed to make the property intensive so that it can be tabulated in a useful manner.

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature (think Charles' Law!) whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature. (For example, If mercury or alcohol didn't expand with increasing temperature, we wouldn't be able to use those substances in thermometers.)

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

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

As was the case with the compressibility factor, the $1/V$ term is needed to make the property intensive, and thus able to be tabulated in a useful fashion. In the case of expansion, volume tends to increase with increasing temperature, so the partial derivative is positive.

Deriving an expression for a partial derivative.

Partial Derivative Transformation Type I

Consider a system that is described by three variables, and for which one can write a

mathematical constraint on the variables

$$F(x, y, z) = 0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions:

$$z(x, y) \quad \text{and} \quad y(x, z)$$

This allows one to write the total differentials for dz and dy as follows

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Substituting the second expression into the first,

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right] \\ dz &= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz \end{aligned}$$

If the system undergoes a change following a pathway where x is held constant ($dx = 0$), this expression simplifies to

$$dz = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

And so for changes for which $dz \neq 0$,

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

This reciprocal rule is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. Begin by writing

$$z(x, y) \rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dz and constrain to constant x .

$$\left. \frac{dz}{dz} \right|_x = \left(\frac{\partial z}{\partial x} \right)_y \left. \frac{dx}{dz} \right|_x + \left(\frac{\partial z}{\partial y} \right)_x \left. \frac{dy}{dz} \right|_x$$

Noting that

$$\left. \frac{dz}{dz} \right|_x = 1 \quad \text{and} \quad \left. \frac{dx}{dz} \right|_x = 0 \quad \text{and} \quad \left. \frac{dy}{dz} \right|_x = \left(\frac{\partial y}{\partial z} \right)_x$$

The result is

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

or

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

This “formal” method of partial derivative manipulation is convenient and useful, although it is not mathematically rigorous. However, it does work for the kind of partial derivatives encountered in thermodynamics because the variables are state variables and the differentials are exact.

Deriving an expression for a partial derivative.

Partial Derivative Transformation Type II

Consider a system that is described by three variables, and for which one can write a mathematical constraint on the variables

$$F(x, y, z) = 0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions:

$$z(x, y) \quad \text{and} \quad y(x, z)$$

This allows one to write the total differentials for dz and dy as follows

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz$$

Substituting the second expression into the first,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right]$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

If the system undergoes a change following a pathway where z is held constant ($dz = 0$), this expression simplifies to

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx$$

And so for and changes in which $dx \neq 0$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This cyclic permutation rule is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. Begin by writing

$$z(x,y) \rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dx and constrain to constant z .

$$\left.\frac{dz}{dx}\right|_z = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dx}\right|_z + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dx}\right|_z$$

Note that

$$\left.\frac{dz}{dx}\right|_z = 0 \quad \text{and} \quad \left.\frac{dx}{dx}\right|_z = 1 \quad \text{and} \quad \left.\frac{dy}{dx}\right|_z = \left(\frac{\partial y}{\partial x}\right)_z$$

The expression now becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

which is easily rearranged to

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics.

Example:

Derive an expression for $\frac{\alpha}{\kappa_T}$.

From the definitions:

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

So

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

Simplifying (canceling the 1/V terms and using transformation Type I to invert the partial derivative in the denominator) yields

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

Applying Transformation Type II give the final result:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T} \right)_V$$

The Joule Experiment

Going back to the expression for changes in internal energy that stems from assuming that U is a function of V and T (or U(V, T) for short)

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

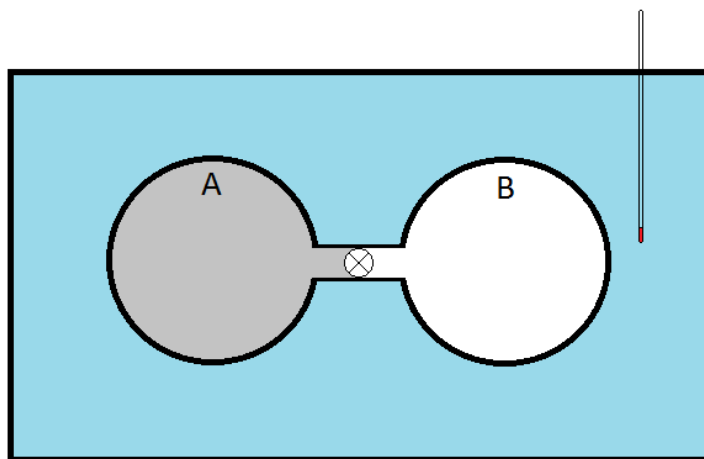
one quickly recognizes one of the terms as the constant volume heat capacity, C_V . And so the expression can be re-written

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

But what about the other term? What is $\left(\frac{\partial U}{\partial V} \right)_T$? The partial derivative is a coefficient called the “internal pressure”, and given the symbol π_T .

$$\pi_T \equiv \left(\frac{\partial U}{\partial V} \right)_T$$

James Prescott Joule (1818-1889) (Encyclopedia Britannica, 2016) recognized that π_T should have units of pressure (Energy/volume = pressure) and designed an experiment to measure it.



He immersed two copper spheres, A and B, connected by a stopcock. Sphere A is filled with a sample of gas while sphere B was evacuated. The idea was that when the stopcock was opened, the gas in sphere A would expand ($\Delta V > 0$) against the vacuum in sphere B (doing no work since $p_{\text{ext}} = 0$). The change in the internal energy could be expressed

$$dU = \pi_T dV + C_V dT$$

But also, from the first law of thermodynamics

$$dU = dq + dw$$

Equating the two

$$\pi_T dV + C_V dT = dq + dw$$

and since $dw = 0$

$$\pi_T dV + C_V dT = dq$$

Joule concluded that $dq = 0$ (and $dT = 0$ as well) since he did not observe a temperature change in the water bath which could only have been caused by the metal spheres either absorbing or emitting heat. And because $dV > 0$ for the gas that underwent the expansion into an open space, π_T must also be zero! In truth, the gas did undergo a temperature change, but it was too small to be detected within his experimental precision. Later, we (once we develop the Maxwell Relations) will show that

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

For an ideal gas $p = RT/V$, so it is easy to show that

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

So

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

And since $RT/V = p$

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

So while Joule's observation was consistent with limiting ideal behavior, his result was really an artifact of his experimental uncertainty masking what actually happened.

For a van der Waals gas,

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

So

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

And

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

Substitution of the expression for p into this relationship yields

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

In general, it can be shown that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

And so the internal pressure can be expressed entirely in terms of measurable properties

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

and need not apply to only gases!

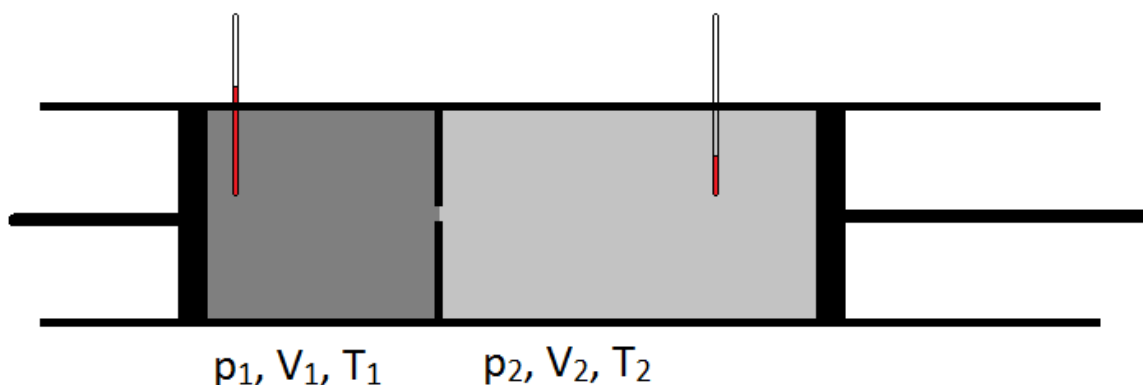
The Joule-Thomson Effect

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a constriction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the constriction. The cooling that they observed as the gas expanded from a high pressure region to a lower pressure region was extremely important and led to a common design of modern refrigerators.

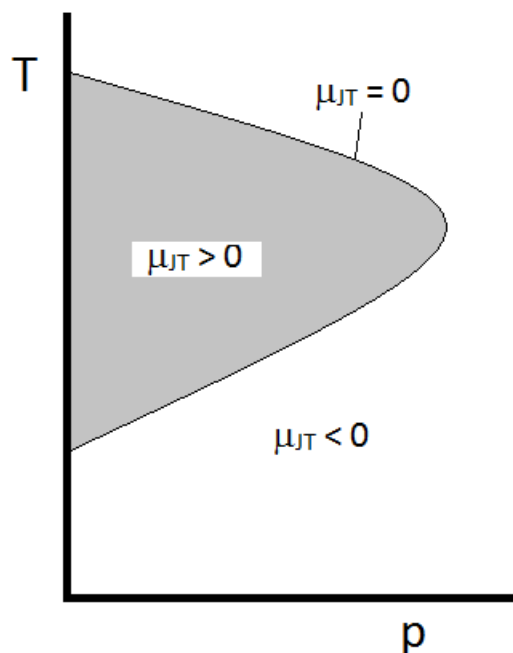
Not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT} . This coefficient has the definition

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

Schematically, the Joule-Thomson coefficient can be measured by measuring the temperature drop or increase a gas undergoes for a given pressure drop. The apparatus is insulated so that no heat can be transferred in or out, making the expansion isenthalpic.



The typical behavior of the Joule-Thomson coefficient can be summarized in the following diagram. At the combinations of T and p for which $\mu_{JT} > 0$ (inside the shaded region), the sample will cool upon expansion. At those p and T conditions outside of the shaded region, where $\mu_{JT} < 0$, the gas will undergo a temperature increase upon expansion. And along the boundary, a gas will undergo neither a temperature increase nor decrease upon expansion. For a given pressure, there are typically two temperatures at which μ_{JT} changes sign. These are the upper and lower inversion temperatures.



Using the tools of mathematics, it is possible to express the Joule-Thomson coefficient in terms of measurable properties. Consider enthalpy as a function of pressure and temperature: $H(p, T)$. This suggests that the total differential dH can be expressed

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

It will be shown later (again, once we develop the Maxwell Relations) that

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

A simple substitution shows

$$\left(\frac{\partial H}{\partial p}\right)_T = -TV\alpha + V = V(1 - T\alpha)$$

So

$$dH = V(1 - T\alpha)dp + C_p dT$$

For an ideal gas, $\alpha = 1/T$, so

$$dH = V\left(1 - T\frac{1}{T}\right)dp + C_p dT$$

which causes the first term to vanish. So for constant enthalpy expansion ($dH = 0$), there can be no change in temperature ($dT = 0$). This will mean that gases will only show non-zero values for μ_{JT} only because they deviate from ideal behavior!

Example:

Derive an expression for μ_{JT} in terms of α , C_p , V , and T .

Solution: Using $H(p, T)$:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

Dividing by dp and constraining to constant H :

$$\left.\frac{dH}{dp}\right|_H = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dp}\right|_H + \left(\frac{\partial H}{\partial T}\right)_p \left.\frac{dT}{dp}\right|_H$$

Noting that $\left.\frac{dH}{dp}\right|_H = 0$, $\left.\frac{dp}{dp}\right|_H = 1$, and $\left.\frac{dT}{dp}\right|_H = \left(\frac{\partial T}{\partial p}\right)_H$

$$0 = \left(\frac{\partial H}{\partial p}\right)_T + \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H$$

We can then use the following substitutions:

$$\begin{aligned}\left(\frac{\partial H}{\partial p}\right)_T &= V(1 - T\alpha) \\ \left(\frac{\partial H}{\partial T}\right)_p &= C_p \\ \left(\frac{\partial T}{\partial p}\right)_H &= \mu_{JT}\end{aligned}$$

To get

$$0 = V(1 - T\alpha) + C_p\mu_{JT}$$

And solving for μ_{JT} gives

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

Useful Definitions and Relationships

In this chapter (and in the previous chapter), several useful definitions have been stated. The following “measurable quantities” have been defined:

$$\begin{aligned}C_V &\equiv \left(\frac{\partial U}{\partial T}\right)_V & \text{and} & & C_p &\equiv \left(\frac{\partial H}{\partial T}\right)_p \\ \alpha &\equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p & \text{or} & & \left(\frac{\partial V}{\partial T}\right)_p &= V\alpha \\ \kappa_T &\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T & \text{or} & & \left(\frac{\partial V}{\partial p}\right)_T &= -V\kappa_T\end{aligned}$$

The following relation has been derived:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V$$

And the following relationships were given without proof (yet!):

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V$$

Together, these relationships and definitions make a powerful set of tools that can be used to derive a number of very useful expressions.

Example:

Derive an expression for $\left(\frac{\partial H}{\partial V}\right)_T$ in terms of measurable quantities.

Solution 1:

Begin by using $H(p, T)$:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

Divide by dV and constrain to constant T (to generate the partial of interest on the left):

$$\left.\frac{dH}{dV}\right|_T = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dV}\right|_T + \left(\frac{\partial H}{\partial T}\right)_p \left.\frac{dT}{dV}\right|_T$$

The last term on the right will vanish (since $dT = 0$ for constant T). After converting to partial derivatives

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

This result is simply a demonstration of the “chain rule” on partial derivatives! But now we are getting somewhere. We can now substitute for $\left(\frac{\partial H}{\partial p}\right)_T$ using our “toolbox of useful relationships”:

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

Using the distributive property of multiplication, this expression becomes

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

Using the cyclic permutation rule (Transformation Type II), the middle term can be simplified

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

And now all of the partial derivatives on the right can be expressed in terms of α and κ_T (along with T and V , which are also “measurable properties”).

$$\left(\frac{\partial H}{\partial V}\right)_T = T \frac{\alpha}{\kappa_T} + V \frac{1}{-V\kappa_T}$$

or

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

Example:

Given

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

Calculate ΔH for the isothermal compression of ethanol which will decrease the molar volume by 0.010 L/mol at 300 K. (For ethanol, $\alpha = 1.1 \times 10^{-3} \text{ K}^{-1}$ and $\kappa_T = 7.9 \times 10^{-5} \text{ atm}^{-1}$).

$$\Delta H = \left(\frac{\partial H}{\partial V}\right)_T \Delta V$$

$$\Delta H = \left[\frac{1}{\kappa_T} (T\alpha - 1) \right] \Delta V$$

$$\Delta H = \left[\frac{1}{7.9 \cdot 10^{-5} \text{ atm}^{-1}} ((300 \text{ K})(1.1 \cdot 10^{-3} \text{ K}^{-1}) - 1) \right] \left(-0.0100 \frac{\text{L}}{\text{mol}} \right)$$

$$\Delta H = 84.81 \frac{\text{atm L}}{\text{mol}} \cdot \frac{8.314 \text{ J}}{0.08206 \text{ atm L}} = 8590 \frac{\text{J}}{\text{mol}}$$

References

Encyclopedia Britannica. (2016). Retrieved March 15, 2016, from James Prescott Joule: English Physicist: <http://www.britannica.com/biography/James-Prescott-Joule>

Vocabulary and Concepts

Euler relation.....	80	isothermal compressibility	81
exact differential	80	Joule-Thomson coefficient.....	88
internal pressure	86	total differential.....	79
isobaric thermal expansivity	81		

Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Express the total differential of a thermodynamic function in terms of partial differentials involving two independent state variables:

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

2. Utilize the Euler relation to define an exact differential.
3. Derive and utilize partial differential transformation types I and II:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

And

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

4. Define and describe the meaning of the **isobaric thermal expansivity** coefficient (α) and the **isothermal compressibility** coefficient (κ_T).
5. Derive expressions for α and κ_T for gases based on an assumed equation of state.
6. Define **internal pressure** and describe the experiment Joule used to attempt to measure it.
7. Calculate a value for the internal pressure based on α and κ_T for a given substance.
8. Derive an expression for the internal pressure of a gas based on an assumed equation of state, given

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

9. Demonstrate that the internal pressure of an ideal gas is zero.
10. Define and describe the physical meaning the Joule-Thomson coefficient.

11. Derive an expression for the Joule-Thomson coefficient in terms of α , C_p , V , and T given

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

12. Demonstrate that the Joule-Thomson coefficient for an ideal gas is zero.
 13. Derive expressions for the temperature and pressure dependence of enthalpy and internal energy in terms of measurable properties. Use these expressions to calculate changes in enthalpy and internal energy for specific substances based on the values of those measurable properties when the temperature or pressure is changed.

Problems

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.

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

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

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 the molar heat capacity is $C_V = 3/2 R$. 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.
4. Given the following data, calculate the change in volume for 50.0 cm³ of a) neon and b) copper due to an increase in pressure from 1.00 atm to 0.750 atm at 298 K.

Substance	κ_T (at 1.00 atm and 298 K)
Ne	1.00 atm ⁻¹
Cu	0.735 x 10 ⁻⁶ atm ⁻¹

5. Consider a gas that follows the equation of state

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

derive an expression for

- the isobaric thermal expansivity, α
- the Joule-Thomson coefficient, μ_{JT}

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

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.

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 $\left(\frac{\partial U}{\partial T}\right)_p$.

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

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

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 .

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

Chapter 4 – Putting the First Law to Work

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

9. Evaluate the expression you derived in problem 8 for an ideal, assuming that the internal pressure of an ideal gas is zero.
10. A van der Waals gas follows the equation of state

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

In this problem, we will derive the expression for the internal pressure of a van der Waals gas.

- a. Find an expression for α/κ_T for a van der Waals gas. $\left(\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V\right)$
- b. Using the expression

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

evaluate π_T .

11. Using your result from problem 10, derive an expression for $\left(\frac{\partial T}{\partial V}\right)_U$ for a van der Waals gas.