# Chapter 4: Putting the First Law to Work

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

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:

Because thermodynamics is kind enough to deal in a number of state variables, the functions that define how those variable 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 suggests that the internal energy depends very intimately on two variables: volume and temperature. In fact, we will se 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) or 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 easy to see how it changes when either (or both!) are changed. This can be written as a **total differential**.

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

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

In general, if a differential can be expressed as

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

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

The total differential of p can be written

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

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 (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 uncompressible! 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.

The negative sign is important in order to keep the value of 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 ()

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

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.

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| **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) and y(x,z)  This allows one to write the total differentials for dz and dy as follows  and  Substituting the second expression into the first,  If the system undergoes a change following a pathway where x is held constant (dx = 0), this expression simplifies to  And so for changes for which dz ≠ 0,  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) 🡺  Now, divide both sides by dz and constrain to constant x.  Noting that  and and  The result is  or  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. |

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| **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) and y(x,z)  This allows one to write the total differentials for dz and dy as follows  and  Substituting the second expression into the first,  If the system undergoes a change following a pathway where z is held constant (dz = 0), this expression simplifies to  And so for and changes in which dx ≠ 0  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) 🡺  Now, divide both sides by dx and constrain to constant z.  Note that  and and  The expression now becomes  which is easily rearranged to  This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics. |

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| **Example**:  Derive an expression for .  From the definitions:  and  So  Simplifying (canceling the 1/V terms and using transformation Type I to invert the partial derivative in the denominator) yields  Applying Transformation Type II give the final result: |

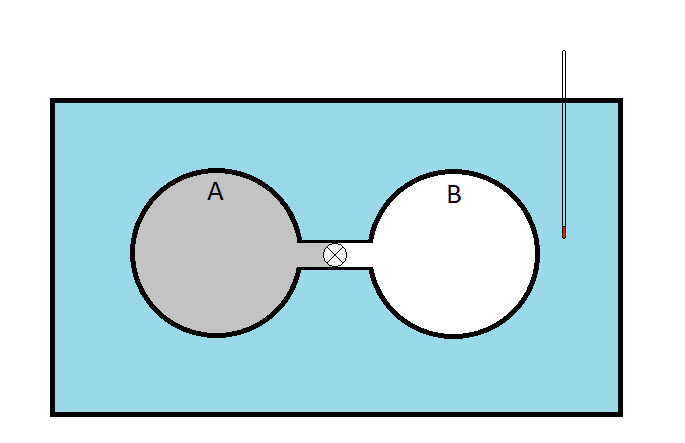
## The Joule Experiment

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)

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

But what about the other term? What is ? The partial derivative is a coefficient called the “internal pressure”, and given the symbol T.

James Prescott Joule (1818-1889) (Encyclopedia Brittannica, 2016) recognized that 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 (V > 0) against the vacuum in sphere B (doing no work since pext = 0. The change in the internal energy could be expressed

But also, from the first law of thermodynamics

Equating the two

and since dw = 0

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, 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

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

So

And since RT/V = p

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,

So

And

Substitution of the expression for p into this relationship yields

In general, it can be shown that

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

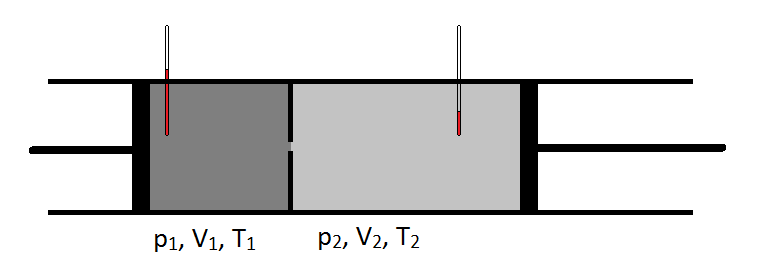
and need not apply to only gases!

## The Joule-Thomson Effect

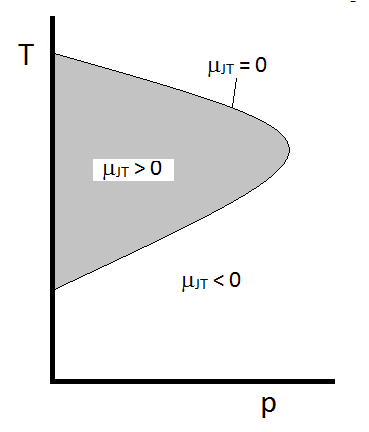
In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream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

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 JT > 0 (inside the shaded region), the sample will cool upon expansion. At those p and T conditions outside of the shaded region, where JT < 0, the gas will undergo a temperature increase upon expansion. And along the boundary, a gas will undergo neither a temperature increase not decrease upon expansion. For a given pressure, there are typically two temperatures at which 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

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

A simple substitution shows

So

For an ideal gas,  = 1/T, so

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 JT only because they deviate from ideal behavior!

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| **Example**:  Derive an expression for JT in terms of , Cp, V, and T.  **Solution**: Using H(p, T):  Dividing by dp and constraining to constant H:  Noting that , and  We can then use the following substitutions:  To get  And solving for JT gives |

## 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:

and

or

or

The following relation has been derived:

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

and

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

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| **Example**:  Derive an expression for in terms of measurable quantities.  Solution 1:  Begin by using H(p, T):  Divide by dV and constrain to constant T (to generate the partial of interest on the left):  The last term on the right will vanish (since dT = 0 for constant T). After converting to partial derivatives  This result is simply a demonstration of the “chain rule” on partial derivatives! But now we are getting somewhere. We can now substitute for using our “toolbox of useful relationships”:  Using the distributive property of multiplication, this expression becomes  Using the cyclic permutation rule (Transformation Type II), the middle term can be simplified  And now all of the partial derivatives on the right can be expressed in terms of a and kT (along with T and V, which are also “measurable properties”.  or |

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| **Example**:  Given  Calculate H for the isothermal compression of ethanol which will decrease the molar volume by 0.010 L/mol at 300 K. (For ethanol,  = 1.1 x 10-3 K-1 and T = 7.9 x 10-5 atm-1). |

# References

*Encyclopedia Brittannica*. (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

exact differential 80

internal pressure 86

isobaric thermal expansivity 81

isothermal compressibility 81

Joule-Thomson coefficient 88

total differential 79

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

And

1. Define and describe the meaning of the **isobaric thermal expansivity** coefficient () and the **isothermal compressibility** coefficient (T).
2. Derive expressions for  and T for gases based on an assumed equation of state.
3. Define **internal pressure** and describe the experiment Joule used to attempt to measure it.
4. Calculate a value for the internal pressure based on  and T­ for a given substance.
5. Derive an expression for the internal pressure of a gas based on an assumed equation of state, given
6. Demonstrate theat the internal pressure of an ideal gas is zero.
7. Define and describe the physical meaning the Joule-Thomson coefficient.
8. Derive an expression for the Joule-Thomson coefficient in terms of , Cp, V, and T given
9. Demonstrate that the Joule-Thomson coefficient for an ideal gas is zero.
10. 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

show that

for an ideal gas.

1. Determine if the following differential is exact, and if so, find the function z(x, y) that satisfies the expression.
2. For a van der Waals gas, . Find an expression in terms of *a*, *n*, *V*, and *R* for if the molar heat capacity is 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.
3. 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.

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

1. Consider a gas that follows the equation of state

derive an expression for

1. the isobaric thermal expansivity, 
2. the Joule-Thomson coefficient, JT
3. 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.

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 .

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, 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 .

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

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

1. Find an expression for T for a van der Waals gas.
2. Using the expression

evaluate T.

1. Using your result from problem 10, derive an expression for for a van der Waals gas.