

3.1: Enthalpy and Changing Functions

Internal energy is not as important in constant pressure (i.e. volume-changing) systems due to the fact that some work energy is in play. As a result, some of the system's energy is gained or lost by the contraction or expansion of the vessel that the gas is in. As a result, we should define another type of energy that is more useful for describing constant pressure systems, which we will call enthalpy (H):

$$H = U + PV \quad (3.1.1)$$

One simple description of enthalpy is that it accounts for the ability to do work as represented by the addition of PV in Equation 3.1, which has units of Joules. As in all things, we are not concerned with thermodynamic variables but changes in those variables during dynamic processes. This prompts us to review the mathematics of change, which are calculus derivatives. The change in P times V prompts the use of the product rule defined as:

$$\frac{\partial (f(x) \cdot g(x))}{\partial x} = f(x) \frac{\partial g(x)}{\partial x} + g(x) \frac{\partial f(x)}{\partial x} \quad (3.1.2)$$

We will use the following symbology to describe Equation 3.2, which is common in multivariable calculus:

$$\partial (f \cdot g) = f \cdot \partial g + g \cdot \partial f \quad (3.1.3)$$

When Equation 3.3 is applied to our new function enthalpy we find:

$$\partial H = \partial U + \partial (P \cdot V) = \partial U + V \partial P + P \partial V \quad (3.1.4)$$

Since we are concerned with constant pressure systems, meaning $\partial P = 0 \text{ Pa}$:

$$\partial H = \partial U + P \partial V \quad (3.1.5)$$

This relationship reveals the utility of enthalpy. First, since U is a state function we can calculate the change in U , i.e. $\partial U = \partial q + \partial w$, any way we want. As such, we will use the reversible path which means $\partial w = -P \partial V$ and as a result: $\partial U = \partial q - P \partial V$. We find after inserting this expression into Equation 3.5: $\partial H = \partial q - P \partial V + P \partial V = \partial q$

Enthalpy is heat! In fact, you probably already knew this, because in Freshman Chemistry we told you that the difference in endothermic and exothermic processes depends on a positive or negative ΔH . Did you just say "Ah-ha I always knew that enthalpy was the heat of a reaction!"? But didn't you learn the same thing about internal energy in the previous chapter? Isn't it true that endo/exothermic is determined by U so long as volume is constant? It is- this is not a trick question- the heat of a reaction is the change of internal energy at constant V , while heat is the change in enthalpy when at constant P .

So, you might feel that you have been lied to, which, you have. But why? To answer, go outside and look up. Do you see a metal box containing the entire planet's atmosphere at a constant volume? No? Then the Earth is a constant pressure system. Now think back to your lab courses. How often was it true that you set up a reaction in a fully enclosed vessel? Note a Schlenk line found in a real research lab aren't enclosed- they have valves that relieve a buildup of pressure for safety's sake. This brings us to our point, which is that it is very rare for chemical processes to be performed at constant volume. Nature doesn't do it, and chemists who care about life and limb also don't do it. Thus, in your earlier learnings about thermodynamics, we stated that endo/exothermicity is due to enthalpy because that is generally true. But not always.

3.1.1 Calculating Enthalpy

Regardless of whether we are studying isothermal or adiabatic processes at constant pressure or volume, you can always calculate the change in enthalpy from Equation 3.4: $\partial H = \partial U + \partial (P \cdot V)$. First, let's tackle isothermal transitions, both reversible and irreversible. Starting with ∂U , we already learned that $\partial U = 0 \text{ J}$ at constant T because of the Equipartition theorem; internal energy can only change if temperature changes. Oddly, this is consistent with the adiabatic formula for changing internal energy: $\partial U = C_V \partial T$, which is likewise 0 J under isothermal conditions ($\partial T = 0 \text{ K}$). The formula $\partial U = C_V \partial T$ works for both isothermal and adiabatic transitions because ∂U is an exact differential, and as a result we can simplify our formula for changing enthalpy: $\partial H = C_V \partial T + \partial (P \cdot V)$. Next, we must figure out what to do with the $\partial (P \cdot V)$ term, which is a bit complex because both P and V may be simultaneously changing for some situations. However, there is an easy way to resolve this; given that we are presently focused on gases we can use the perfect gas law to find:

$$\partial (P \cdot V) = nR \partial T \quad (3.1.6)$$

which is true because we assume both n (moles) and R ($=8.314 \text{ J/K/mol}$) are constants. This leaves us with:

$$\partial H = C_V \partial T + nR \partial T = (C_V + nR) \partial T \quad (3.1.7)$$

We will use Equation 3.6 for many problems, and as it applies here it shows that $\partial H = 0 \text{ J}$ for isothermal processes regardless of whether the path is reversible or irreversible.

Under adiabatic conditions there is thermal insulation covering the reactor vessel or piston, which means heat or work results in a temperature change. Thus, to calculate the change in enthalpy for adiabatic changes one first determines the change in temperature ΔT from Equation 2.14 (reversible) or Equation 2.15 (irreversible) and use that result into the integrated form of Equation 3.7: $\Delta H = (C_V + nR) \Delta T$. This will also apply to both reversible and irreversible adiabatic transitions since ∂H is exact. As we pointed out in Ch. 2 that $C_P = C_V + nR$, which we will prove rigorously below, it is also true that $\Delta H = C_P \Delta T$.

3.1.2 Proofs. Up or down?

The purpose of thermodynamic proofs is to determine relationships between variables that are not immediately obvious. For example, does internal energy (U) rise or fall with increasing volume under adiabatic conditions (i.e. $\partial q = 0 \text{ J}$)? This is such a specific question I cannot instinctually answer. However, if we do a formal derivation then we can figure this out. Starting with:

$$\partial U = \partial w + \partial q = -P \partial V$$

we can divide by the change in volume and hold the heat (q) constant:

$$\left(\frac{\partial U}{\partial V} \right)_q = -P \left(\frac{\partial V}{\partial V} \right)_q = -P$$

where we used the fact that $\left(\frac{\partial V}{\partial V} \right)_q = 1$. As pressure is always positive, $-P$ is always negative, and thus internal energy always decreases with increasing volume under adiabatic conditions. Note that we designate heat (q) as constant in the partial derivatives, i.e. $\left(\frac{\partial U}{\partial V} \right)_q$ and $\left(\frac{\partial V}{\partial V} \right)_q$, thus, it isn't "just P or V that can be held constant in thermodynamic proofs. We can hold anything we want constant.

Hopefully you see the value of thermodynamic proofs, after all how else could you have answered this question? However, perhaps this is more obvious than you realized given what you know about adiabatic transitions. Since a piston is thermally insulated, and volume increases, then the temperature will decrease. Don't your instincts tell you that a gas cools upon expansion? And since you know that decreasing the temperature will decrease the internal energy according to the Equipartition theorem, then it makes sense that $\left(\frac{\partial U}{\partial V} \right)_q$ is negative! Example problems 3.1 and 3.2 are provided to give you some more practice with proofs.

You may have noticed that work, $\partial w = -P_{ext} \partial V$, is always assumed to be reversible: $\partial w = -P \partial V$ in just about every example of calculating or deriving ∂U or ∂H . This is because these energies are state functions, and their differentials are exact and path independent. As a result, we can always use reversible work in these derivations, which makes the effort significantly simpler. We don't have to use irreversible work, even if the process under scrutiny is irreversible, since we would still determine the same ∂U or ∂H . Using the irreversible definition is tantamount to intentionally make these derivations more complex.

3.2 Heat Capacities.
3.3 Natural Variables and Legendre Transforms. **3.4 The Joule and Joule-Thomson Experiments.** Back in early 1800's, Sir James Joule was a somewhat well-off brewer who became interested in using mechanical means to produce heat. The problem was that no one thought that work could become heat, despite the fact that this is incredibly obvious to anyone who rubs their hands together in the cold. Joule was able to perform fairly sophisticated measurements to show that work does indeed transform to heat, sometimes using contraptions nearly the size of a house. Ultimately, Joule's efforts led to the 1st Law of Thermodynamics.

Part of Joule's research centered on testing thermodynamic theories, especially concerning work and heat. For example- we all know that an expanding gas gets cold. Or does it? First, imagine a thermally insulated system (i.e. adiabatic, so $\partial q = 0 \text{ J}$ which should be a knee-jerk reaction for you when "adiabatic" is stipulated). Inside of this device is a pressurized container connected with a valve to another vessel under vacuum; this is shown in Figure 3.1. If the gas cools when the valve opens and the gas expands into the vacuum, then there should be a decrease in the surrounding water temperature as measured by the thermometer. Of course, our instincts tell us that the expanding gas will cool, and the water will chill.

Joule did this experiment and oddly the water temperature didn't change at all! However, later the experiment was repeated with better equipment and it was found that the water bath did cool, just not very much. And it gets more interesting- if you use hydrogen or helium, the water *gets slightly warmer*. It seems that this system is much more complicated than originally though! To delve deeper, we need to determine how temperature changes when a gas increases its volume: $\left(\frac{\partial T}{\partial V}\right)_?$, but it isn't clear what variable is held constant in the Joule contraption. We can figure this out in several steps, first noting that the gas expands into a vacuum ($P_{ext} = 0 \text{ Pa}$). As a result, the work of expansion is $\partial w = -P_{ext} \partial V = 0 \text{ J}$. And $\partial q = 0 \text{ J}$ due to the adiabatic conditions, which makes $\partial U = \partial w + \partial q = 0 \text{ J}$; thus the expansion occurs under conditions of constant internal energy. Consequently, the Joule experiment measures the change in volume under constant internal energy conditions, i.e. $\left(\frac{\partial T}{\partial V}\right)_U$. Now we will use a math identity called the Euler Chain formula, Equation 3.11, which is derived on the previous page if you're interested. We will start with:

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

and apply it to $\left(\frac{\partial T}{\partial V}\right)_U$, where $x = T$, $y = V$ and $z = U$: $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T$. Recall that $\partial U = C_V \partial T$ and thus $\frac{1}{C_V} = \left(\frac{\partial T}{\partial U}\right)_V$, which allows us to summarize:

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \cdot \left(\frac{\partial U}{\partial V}\right)_T \quad (3.1.8)$$

where μ_J is called the Joule coefficient.

Now we see why the Joule experiment is so odd. Since it is setup such that $\partial U = 0 \text{ J}$, then there should be no change in temperature because $\partial U = C_V \partial T$. The Joule coefficient (μ_J) likewise should be $\sim 0 \text{ K/m}^3$ since it is equal to $\left(\frac{\partial T}{\partial V}\right)_U$ and we expect $\partial T = 0 \text{ K}$. However, note that we stated that the change in temperature was not *exactly* zero, it was only *close* to 0 K. This behavior can be understood when we view the Joule coefficient as $\mu_J = -\frac{1}{C_V} \cdot \left(\frac{\partial U}{\partial V}\right)_T$. By the end of Chapter 4 you will be able to do a thermodynamic proof to show that $\left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ J/m}^3$ for a perfect gas, but $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ for a van der Waals gas. Consequently, the non-zero Joule coefficient is due to real gas behavior. For example, a real gas differs from a perfect gas because the real gas molecules interact, and now we see that this affects the internal energy. Most gas molecules have energy-lowering self-interactions via the attractive “ a ” parameter as explained in Chapter 1, which means that getting closer as the volume decreases ($\partial V < 0 \text{ m}^3$) lowers the energy ($\partial U < 0 \text{ J}$), resulting in a positive $\left(\frac{\partial U}{\partial V}\right)_T$ which is consistent with from $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ the van der Waals equation. Thus, expanding the gas cools it, just very slightly. However, hydrogen and helium are oddballs- they have very small self interactions and higher compressibility factors. As a result, these gases get warmer when expanded in a Joule apparatus.

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