

3.4: The Joule and Joule-Thomson Experiments

Joule was buddies with Lord Kelvin, or William Thomson as he was known at the time. At first Thomson believed in the “caloric” theory of heat, which is that heat is like mass and can transfer between objects. However, at a scientific conference Joule was able to convince Thomson that heat and work were transferrable, and they set out to test this hypothesis using a different contraption whereby gas was pushed from one vessel through a “throttle” into another. The Joule-Thomson device is shown in Figure 3.2. There are two tricks to this experiment. One is that all the gas is transferred, meaning that all thermodynamic variables are 0 initially for the right side of the container and are 0 in the final state for the left container. This is because no gas has no volume and no energy. The other clever move is that the “throttle” in between the left and right sides allows the gas to be transferred such that the compression on the left and expansion on the right occur at constant pressure.

Let us slow down and analyze the Joule-Thomson experiment in steps. Initially, all the gas is on the left side and has an internal energy of U_1 ; we will say that the gas is in “state 1”. All the gas is transferred to the right side of the device in state 2, so the final internal energy is U_2 . Mathematically all of this is expressed as:

$$\Delta U = \int_{U_1}^{U_2} \partial U = U_2 - U_1$$

The system is adiabatic ($\partial q = 0$ J), which means that the changes in internal energies are entirely due to work. Thus, for both vessels, $\Delta U = \int \partial w$. The total work is the sum of that performed on the left and right sides. The left-side work is easy to calculate because the pressure of the 1st vessel is constant as the plunger is compressed, resulting in:

$$\Delta w_1 = - \int_{V_1}^{0 L} P_1 \cdot \partial V = -P_1 \cdot (0 L - V_1) = P_1 V_1$$

Likewise, the work on the right side is:

$$\Delta w_2 = - \int_{0 L}^{V_2} P_2 \cdot \partial V = -P_2 \cdot (V_2 - 0 L) = -P_2 V_2$$

and the total work is $P_1 V_1 - P_2 V_2$. We can now equate the change in internal energy with the total work:

$$U_2 - U_1 = P_1 V_1 - P_2 V_2$$

thus, $U_2 + P_2 V_2 = U_1 + P_1 V_1$ or $H_2 = H_1$, resulting in $\Delta H = 0$ J. Consequently, the Joule-Thomson experiment is isenthalpic.

As with the Joule experiment, you are probably questioning whether the gas gets hot or cold in the process. Similar to the previous example we will apply $\left(\frac{\partial T}{\partial P}\right)_H$ to the Euler chain: $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$ to determine the Joule-Thomson coefficient:

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T \quad (3.4.1)$$

using the fact that $\left(\frac{\partial T}{\partial H}\right)_P = \frac{1}{C_P}$. Similar to Joule’s experiment, if $\partial H = 0$ J then the transition should be isothermal, i.e. $\partial T = 0$ K. However, depressurizing a gas generally results in a modest cooling which must be due to real gas behavior. The cooling of a gas is much easier under isoenthalpic conditions, and as a result the Joule-Thomson experiment led to modern refrigeration. Shown in Table 3.0 are various Joule-Thomson coefficients, where we can see that most gases have positive coefficients which means that the gas will cool upon depressurization. The effect is rather large for ammonium and Freon, and as before we see that hydrogen is an outlier. Because of ammonia’s large positive μ_{J-T} the first refrigeration plants used ammonium as a coolant, which was as bad an idea because they tended to explode. People then turned to the use of Freon, also known as R22 which is a mixture of chlorofluorocarbons, which was also a bad idea because it destroyed the ozone layer. This is why we use R410A now, which is better than ammonia or Freon; however, it is a powerful greenhouse gas.

Gas	μ_{J-T} (K atm ⁻¹)
Helium	-0.062

Gas	μ_{J-T} (K atm ⁻¹)
air	0.227
CO ₂	1.11
Freon	1.20
NH ₃	3.39

As part of the Chapter 5 homework problems you will demonstrate that $\left(\frac{\partial H}{\partial P}\right)_T = 0 \text{ J/Pa}$ for a perfect gas, while $\left(\frac{\partial H}{\partial P}\right)_T \approx nb - \frac{2na}{RT}$ for a real (van der Waals) gas. To do these derivations you have to learn about entropy and the 2nd Law of Thermodynamics. This also gives you the tools to explore much further advanced thermodynamic derivations.

Conclusion. This chapter has shown you how new equations for energy can be defined by the Legendre Transform. Specifically, Enthalpy was introduced by a simple manipulation of Internal energy, and it has utility when a transformation is performed under constant pressure conditions. But what if temperature isn't constant? As we move forward, we will study changes in temperature and make further use of the Legendre Transform. Of course, we must know what thermodynamic variable is the conjugate of temperature. That just happens to be entropy.

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