

10.2: The Joule Experiment

In Joule's original experiment, there was a cylinder filled with gas at high pressure connected via a stopcock to a second cylinder with gas at a low pressure – sufficiently low that, for the purpose of understanding the experiment, we shall assume the second cylinder to be entirely empty. The two cylinders were immersed in a water bath, and the stopcock was opened so that gas from the high pressure cylinder flowed into the evacuated cylinder. No heat was supplied to or lost from the system, nor did the gas do any work, so the *internal energy* was constant during the expansion. Joule found no temperature fall as a result of the expansion. This, as we have argued in Section 10.1, is exactly what we would expect for an ideal gas; that is, for an ideal gas, the temperature is independent of the volume if the internal energy is constant. That is, for an ideal gas,

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_U}_{\text{Ideal Gas}} = 0. \quad (10.2.1)$$

For a real gas, however, we would expect a small drop in temperature, and $\left(\frac{\partial T}{\partial V}\right)_U$, which is called the **Joule coefficient**, is not zero. The heat capacity of the water bath and the cylinders in Joule's original experiment, however, was too large for him to detect any fall of temperature even with a real gas. More sensitive experiments found that almost all gases cool during a Joule expansion at all temperatures investigated; the exceptions are helium, at temperatures above about 40 K, and hydrogen, at temperatures above about 200 K.

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_U}_{\text{Real Gas}} \neq 0. \quad (10.2.2)$$

We should be able to derive an expression for the Joule coefficient, given the equation of state, and we should also be able to show that, if the equation of state is the equation of state for an ideal gas, the Joule coefficient is zero.

Internal energy and enthalpy are both functions of state; that is, they are functions of P , V and T . However, any particular substance cannot exist at any arbitrary point in PVT -space, but is constrained to be on the two-dimensional surface represented by its *equation of state*. Figures VI.7, 8 and 9 of Chapter 6 represent an example of such a surface. In other words, P , V and T cannot be varied independently; they are connected by an equation of the form $f(P, V, T) = 0$. Thus internal energy and enthalpy can be described by a function of just two of the state variables P , V and T . In the experiment we are discussing, we are interested in how temperature varies with volume in an experiment in which the internal energy is constant. We shall therefore choose U as our state function and V and T as our independent state variables. That is, we shall write $U = U(V, T)$, so that

$$\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1. \quad (10.2.3)$$

Our aim, of course, is to find an expression for the Joule coefficient $\left(\frac{\partial T}{\partial V}\right)_U$, for which I shall be using the symbol η .

The second of these partial derivatives is C_V , and therefore

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left(\frac{\partial U}{\partial V}\right)_T. \quad (10.2.4)$$

Now

$$dU = TdS - PdV. \quad (10.2.5)$$

That is,

$$dS = \frac{1}{T} [dU + PdV] \quad (10.2.6)$$

$$= \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV \right]. \quad (10.2.7)$$

$$= \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT. \quad (10.2.8)$$

But we also have

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT. \quad (10.2.9)$$

Therefore

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \quad (10.2.10)$$

and

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V. \quad (10.2.11)$$

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{T^2} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] + \frac{1}{T} \left[\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial P}{\partial T} \right)_V \right] \quad (10.2.12)$$

and

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T}. \quad (10.2.13)$$

But entropy is a function of state and dS is an **exact differential**, so the mixed second derivatives are equal. Whence, after simplification:

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P. \quad (10.2.14)$$

Hence, returning to Equation 10.2.4, we obtain, for the Joule coefficient,

$$\eta = \left(\frac{\partial T}{\partial V} \right)_U \quad (10.2.15)$$

$$= \frac{1}{C_V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right]. \quad (10.2.16)$$

Exercise 10.2.1

Show that, for an ideal gas, the Joule coefficient is zero.

Example 10.2.1

Show that, for a van der Waals gas, the Joule coefficient is

$$\left(\frac{\partial T}{\partial V} \right)_U = -\frac{a}{C_V V^2}.$$

Hence, for a finite volume change,

$$T_2 = T_1 - \frac{a}{C_V} \left(\frac{1}{V_1} - \frac{1}{V_2} \right).$$

Solution

For example, the volume of a kmole of CO₂ at a temperature of 20 °C (293.15 K) and a pressure of 1 atm (1.013 × 10⁵ Pa) is $V_1 = RT/P = 24.06 \text{ m}^3$. (That's a lot of cubic metres – but then 44 kg of CO₂ is a lot of carbon dioxide.). If its volume were doubled to 48.12 m³ in an irreversible Joule-type expansion, what would be its new temperature? From Chapter 6, we find $a = 3.7 \times 10^5 \text{ Pa m}^6 \text{ kmole}^{-1}$, and from Chapter 8 we find that $C_P = 37100 \text{ J kmole}^{-1} \text{ K}^{-1}$ and therefore let's take $C_V = 28786 \text{ J kmole}^{-1} \text{ K}^{-1}$, and so we obtain $T_2 = 292.88 \text{ K} = 19.73 \text{ °C}$. This cooling is a result not of the gas doing external work as in a reversible adiabatic expansion, but of doing work against the internal van der Waals forces between the molecules. What would

be the temperature drop in a reversible adiabatic expansion? The new temperature would be given by $T_2 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1$. Let's take $\gamma = 37100 \div 28786 = 1.29$. Then $T_2 = (1/2)^{0.29} \times 293.15 = 239.77 \text{ K} = -33.38 \text{ }^\circ\text{C}$ at which temperature it would easily have sublimated into solid CO_2 . In this calculation, I used $C_P - C_V = R$ and $TV^{\gamma-1} = \text{constant}$, which are valid only for an ideal gas. We'll shortly derive a more general expression for $C_P - C_V$, but the correction for nonideality will obviously be quite small.

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