

4.4: 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)

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

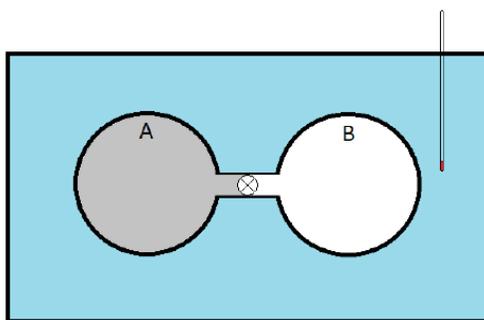
one quickly recognizes one of the terms as the constant volume heat capacity, C_V . And so the expression can be re-written

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

But what about the first term? The partial derivative is a coefficient called the “internal pressure”, and given the symbol π_T .

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

James Prescott Joule (1818-1889) 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 $p_{ext} = 0$). 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

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad (4.4.1)$$

Application to an Ideal Gas

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

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \quad (4.4.2)$$

so combining Equations 4.4.1 and 4.4.2 together to get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - p \quad (4.4.3)$$

And since also because $p = RT/V$, then Equation 4.4.3 simplifies to

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

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.

Application to a van der Waals Gas

For a van der Waals gas,

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (4.4.4)$$

so

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \quad (4.4.5)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V-b} - p \quad (4.4.6)$$

Substitution of the expression for p (Equation 4.4.4) into this Equation 4.4.6

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

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 (real or ideal)!

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