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 \(\pi_T\).

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

James Prescott Joule (1818-1889) recognized that \(\pi_T\) 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, \(\pi_T\) 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

\[ \left( \dfrac{\partial U}{\partial V} \right)_T = T \left( \dfrac{\partial p}{\partial T} \right)_V - p \]

Application to an Ideal Gas

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

\[ \left( \dfrac{\partial p}{\partial T} \right)_V = \dfrac{R}{V} \]

so combining Equations \ref{eq3} and \ref{eq4} together to get

\[ \left( \dfrac{\partial U}{\partial V} \right)_T = \dfrac{RT}{V} - p \]

And since also because \(p = RT/V\), then Equation \ref{eq5} simplifies to

\[ \left( \dfrac{\partial U}{\partial V} \right)_T = p - p = 0 \]

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,

\[ p = \dfrac{RT}{V-b} - \dfrac{a}{V^2} \]

so

\[ \left( \dfrac{\partial p}{\partial T} \right)_V = \dfrac{R}{V-b} \]

and

\[ \left( \dfrac{\partial U}{\partial V} \right)_T = T \dfrac{R}{V-b} - p \]

Substitution of the expression for \(p\) (Equation \ref{eqV1}) into this Equation \ref{eqV3}

\[ \left( \dfrac{\partial U}{\partial V} \right)_T = \dfrac{a}{V^2} \]

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)!

**Contributors**

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