

The Gay-Lussac-Joule Experiment

Thus far, we have only stated that, for objects for which there are only quadratic degrees of freedom, we can write

$$U = \frac{f}{2}NkT \quad (1)$$

That is, the internal thermal energy is a function of temperature *only* ($U = U(T)$). How do we know this? The equation relates macroscopic and microscopic quantities, so it is possible to approach the issue from ‘either end’. However, in this development, I wish to focus on the macroscopic, i.e. what is actually measured in the lab? A famous approach is the *Gay-Lussac-Joule Experiment* (see picture).

In general, we can write $U = U(T, V, P)$ but, since an equation of state should exist (i.e. there exists $P = P(V, T)$), then we only need two variables to completely specify the energy equation, once the relevant equation of state is used. We will choose $U = U(T, V)$, i.e. we start by assuming that U is indeed a function of *both* T and V and go from there. The steps would be as follows:

1. Fill side A with a gas, leaving side B evacuated.
2. Allow the gas to reach thermal equilibrium with the surrounding liquid bath. The bath is insulated so as not to allow any heat transport with the exterior. Once equilibrium is achieved, the temperature, T , (of both bath and gas) is measured and known.
3. Open the valve and let the gas expand (free expansion) so that it finally occupies both sides. No work is done on the gas, i.e. $W = -\int PdV = 0$ because $P = 0$.
4. Allow the gas in the new configuration to reach thermal equilibrium with the bath again. *If* there has been a change in temperature of the gas, then there should be a flow of heat between the gas and the surrounding bath. The result should be a change in temperature of the bath which can then be measured.
5. Measure the temperature of the bath (which is the same as the gas). The experimental result: there is *no* change in temperature¹. Since T remains

¹Actually, the first time this experiment was run, the temperature change was simply too small to be measurable.

constant, there must have been no exchange of heat between the gas and bath; therefore $Q = 0$.

6. Since both $W = 0$ (point 3 above) and $Q = 0$ (point 5) then by the first law of thermodynamics, $dU = 0$ as well, implying that $U = \text{constant}$. We can now conclude that $\frac{\partial T}{\partial V}|_U = 0$.

7. From our circular identity:

$$\frac{\partial U}{\partial V}\Big|_T \frac{\partial V}{\partial T}\Big|_U \frac{\partial T}{\partial U}\Big|_V = -1 \quad (2)$$

$$\therefore \frac{\partial U}{\partial V}\Big|_T = -\frac{\partial U}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_U \quad (3)$$

$$\frac{\partial U}{\partial V}\Big|_T = -C_V \frac{\partial T}{\partial V}\Big|_U \quad (4)$$

8. We know that C_V has a value, so if $\frac{\partial T}{\partial V}\Big|_U = 0$ as we found in point 6 above, then it must also be true that $\frac{\partial U}{\partial V}\Big|_T = 0$.

9. We started by assuming that U could be completely described by $U(T, V)$ so we can now expand the derivative,

$$dU = \frac{\partial U}{\partial V}\Big|_T dV + \frac{\partial U}{\partial T}\Big|_V dT \quad (5)$$

However, we just showed that the first coefficient is zero, so the result is

$$dU = \frac{\partial U}{\partial T}\Big|_V dT = C_V dT \quad (6)$$

An integration over definite limits would give, $U = C_V(T - T_0) + U_0$. That is, $U = U(T)$ *only* (not V). At $T_0 = 0$, there is no internal energy so $U_0 = 0$ in which case $U = C_V T$ which is Eqn. 1 with $C_V = N\frac{f}{2}k$.

Of course, this experiment applies only to an ideal gas but it nicely illustrates how Eqn. 1 can be determined for that circumstance.