Today

I. Last Time

II. Heat Capacities

III. Enthalpy and Thermodynamic Potentials

I. We studied adiabatic compression in some detail. We found

$$VT^{f/2} = \text{const.}$$

On the homework you will show that

$$V^{\gamma}P = \text{const.}$$

Here γ is the `adiabatic exponent' and is defined by

$$\gamma \equiv (f + 2)/f.$$

Definition of heat capacity

$$C \equiv \frac{Q}{\Delta T} \qquad \text{or} \qquad Q = C\Delta T.$$

Henry's guest lecture

$$\ell = \frac{1}{4\pi r^2} \frac{V}{N} \qquad \text{and} \quad Q = -\frac{1}{2}C_V\ell\frac{dT}{dx}$$

II. Heat Capacities

Definition of heat capacity

$$C \equiv \frac{Q}{\Delta T} \qquad \text{or} \qquad Q = C\Delta T.$$

As we said, the heat capacity depends on the material. We also talk about the specific heat capacity of a material,

$$c = \frac{C}{m},$$

It is this latter quantity that is the true material property.

A second important point is that it's ambiguous until you tell me the process that is being undertaken. Let's use the 1st law and we see

$$C = \frac{\Delta U - W}{\Delta T}.$$

Let's consider an isochoric (constant volume) process

$$C_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

II. Heat Capacities

Let's consider an isobaric (constant pressure) process

$$C_P = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U - (-P\Delta V)}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

Let's consider one very special example, the ideal gas,

$$U = \frac{f}{2}NkT,$$

then we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2}Nk = \frac{f}{2}nR.$$

Or, in the case of a constant pressure process,

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \frac{f}{2}Nk + P\frac{Nk}{P} = \frac{f}{2}Nk + Nk = \frac{f+2}{2}Nk.$$
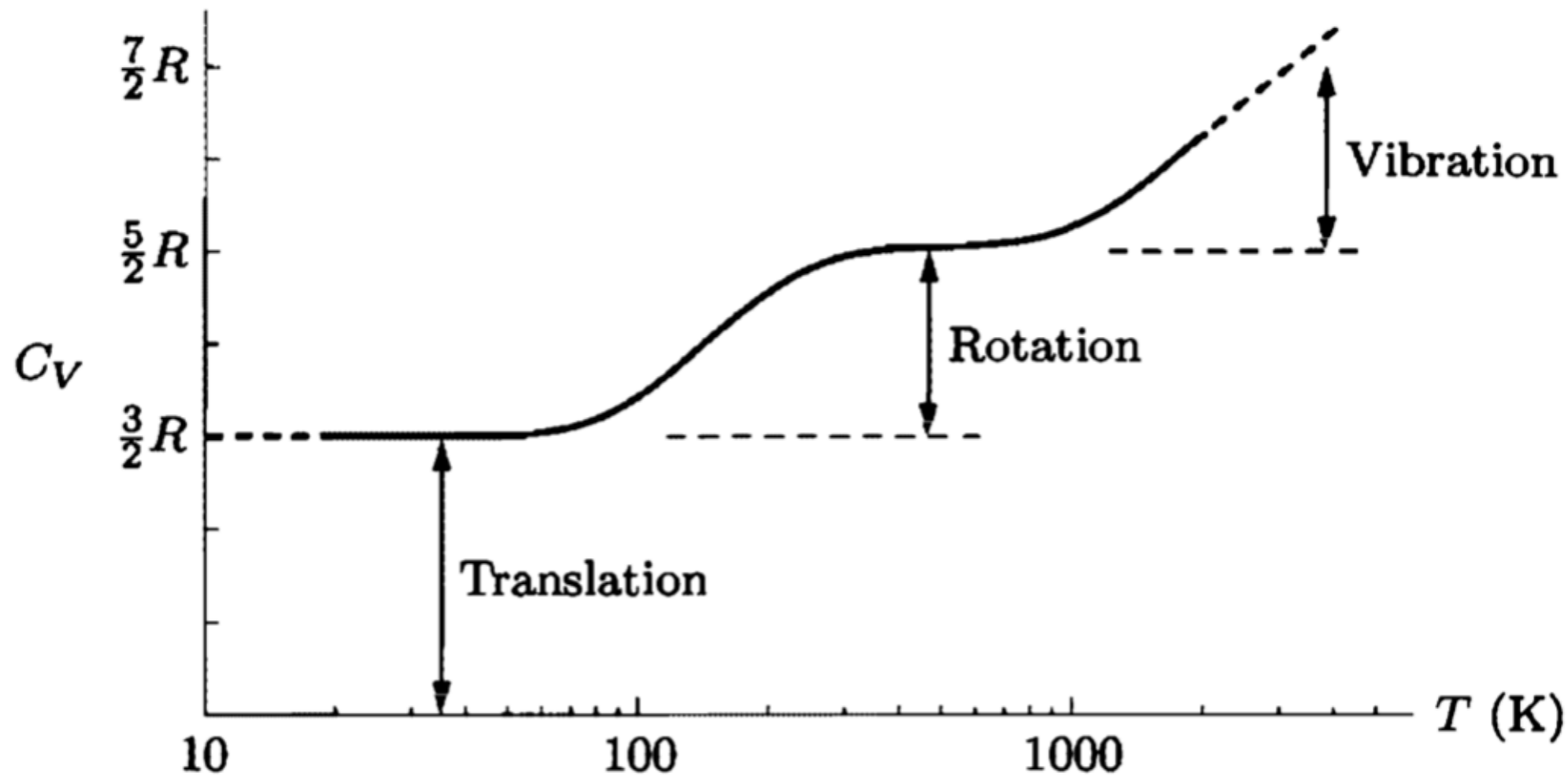
Figure 1.13. Heat capacity at constant volume of one mole of hydrogen (H_2) gas. Note that the temperature scale is logarithmic. Below about 100 K only the three translational degrees of freedom are active. Around room temperature the two rotational degrees of freedom are active as well. Above 1000 K the two vibrational degrees of freedom also become active. At atmospheric pressure, hydrogen liquefies at 20 K and begins to dissociate at about 2000 K. Data from Woolley et al. (1948).
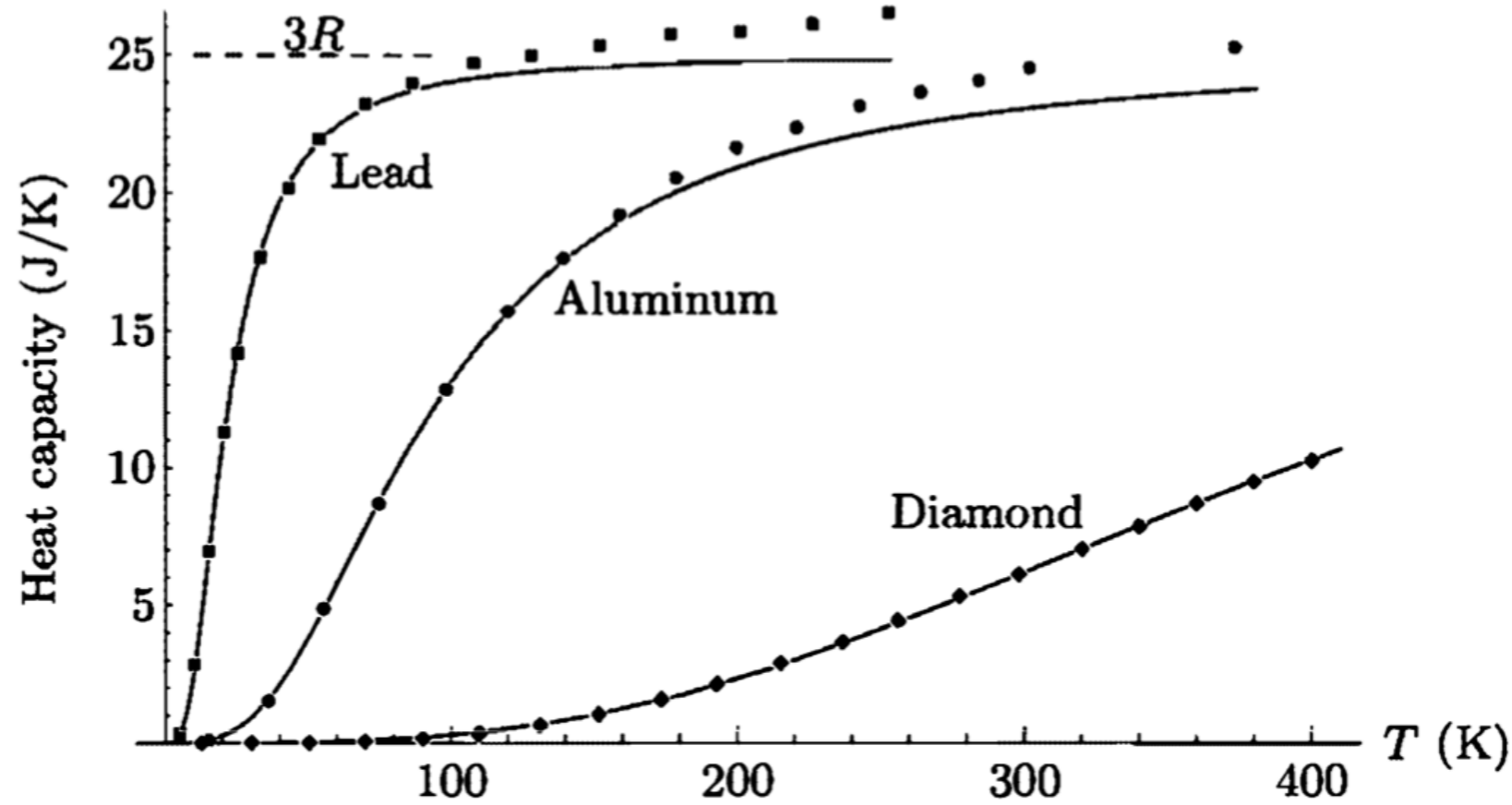
Figure 1.14. Measured heat capacities at constant pressure (data points) for one mole each of three different elemental solids. The solid curves show the heat capacity at constant *volume* predicted by the model used in Section 7.5, with the horizontal scale chosen to best fit the data for each substance. At sufficiently high temperatures, C_V for each material approaches the value $3R$ predicted by the equipartition theorem. The discrepancies between the data and the solid curves at high T are mostly due to the differences between C_P and C_V. At $T = 0$ all degrees of freedom are frozen out, so both C_P and C_V go to zero. Data from Y. S. Touloukian, ed., *Thermophysical Properties of Matter* (Plenum, New York, 1970).

III. Enthalpy

At some point people noticed that it was quite useful to work with a combination of internal energy and pressure & volume:

$$H = U + PV.$$

Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

III. Enthalpy

At some point people noticed that it was quite useful to work with a combination of internal energy and pressure & volume:

$$H = U + PV.$$

Let's imagine doing something to our system, say we add a little heat, when we do that H changes by ΔH, U by ΔU, and V by ΔV.

$$H + \Delta H = (U + \Delta U) + P(V + \Delta V)$$
$$= U + PV + (\Delta U + P\Delta V).$$

Then,

$$\Delta H = \Delta U + P\Delta V \quad (\text{const. } P).$$

Using the 1st law we have

$$\Delta U = Q + (-P\Delta V) + W_{\text{other}},$$

and

$$\Delta H = Q + W_{\text{other}}.$$