

Ch. 1.6 Heat capacities

Heat capacity: amount of heat needed to raise its temperature (1 K),

$$C \equiv \frac{Q}{\Delta T}$$

Specific heat capacity: heat capacity per unit mass,

$$c \equiv \frac{C}{m}$$

The amount of heat needed to raise an object's temperature by 1 K *depends on the circumstances, on whether you're also doing work on the object, as,*

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

Thus we can consider two cases that are most likely to occur,

1st being $W = -P\Delta V = 0$.

1. Heat capacity at constant volume

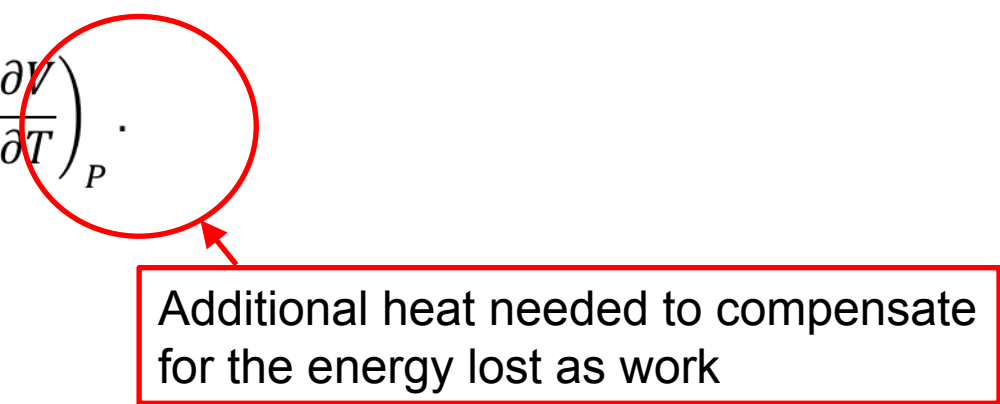
$$C_V \equiv \left(\frac{Q}{\Delta T} \right)_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V .$$

e.g. for a gram of water, $C_V = 1 \text{ cal/}^\circ\text{C} = 4.2 \text{ J/}^\circ\text{C}$

In the usual case objects often expand (so *doing pressure-volume work on the surroundings*) as they are heated.

2. Heat capacity at constant pressure

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



Additional heat needed to compensate
for the energy lost as work

For ideal gas (each molecule having f degrees of freedom),

$$C_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \frac{\partial}{\partial T} \left(\frac{NfkT}{2} \right)_V = \frac{Nfk}{2}.$$

e.g. for 1 mole of monoatomic ideal gas ($f = 3$), $C_V = 3/2 * N_A k = 3/2 R = 12.5 \text{ J/K}$

And for ideal gas,

$$\begin{aligned} C_P &= \left(\frac{\Delta U - (P\Delta V)}{\Delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \\ &= C_V + P \left(\frac{\partial V}{\partial T} \right)_P = C_V + nR. \end{aligned}$$

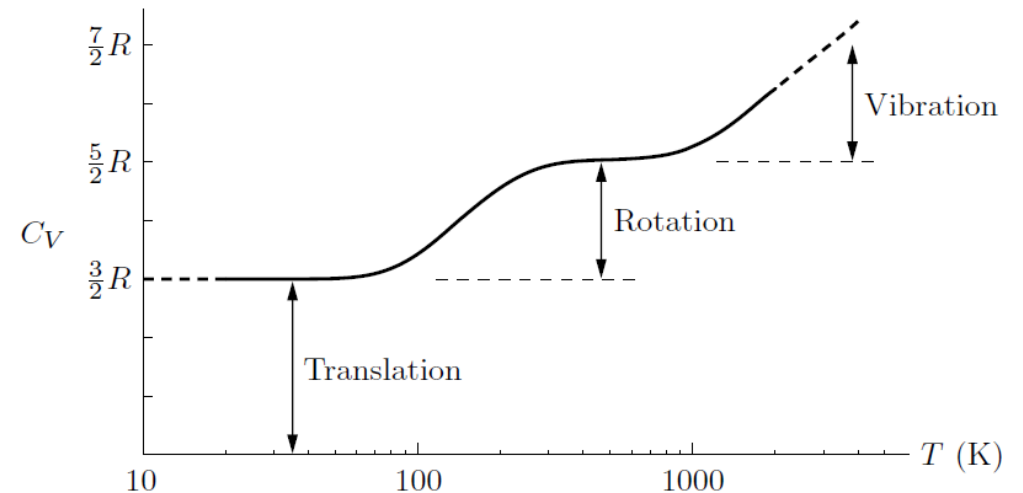


Figure 1.13. Heat capacity at constant volume of one mole of hydrogen (H_2) gas. Note that the temperature scale is logarithmic. Below about 100 K only the three translational degrees of freedom are active. Around room temperature the two rotational degrees of freedom are active as well. Above 1000 K 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). Copyright ©2000, Addison-Wesley.

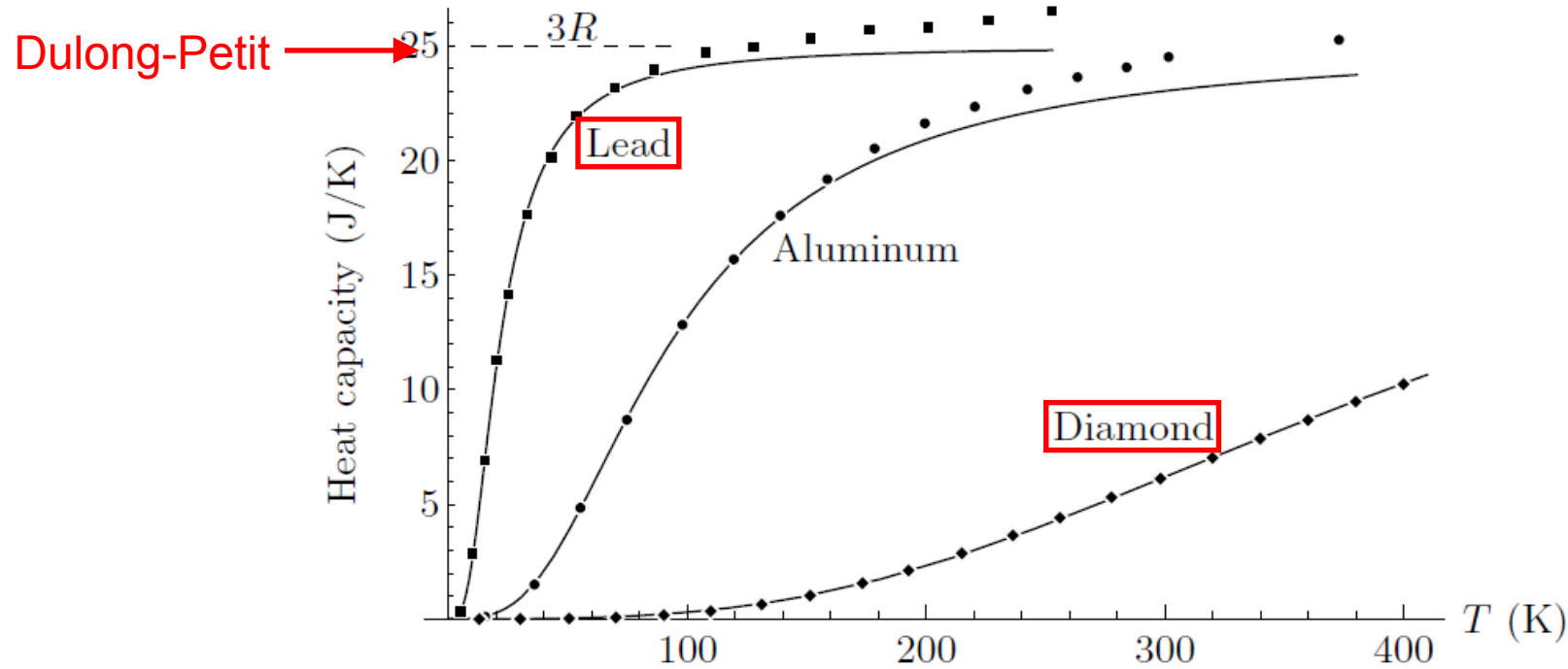


Figure 1.14. Measured heat capacities at constant pressure (data points) for one mole each of three different elemental solids. The solid curves show the heat capacity at constant *volume* predicted by the model used in Section 7.5, with the horizontal scale chosen to best fit the data for each substance. 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). Copyright ©2000, Addison-Wesley.

Latent heat: heat required to melt or boil the substance

$$L \equiv \frac{Q}{m}$$

e.g. for a gram of ice, latent heat for melting: 333 J/g = 80 cal/g

for a gram of water, latent heat for boiling: 2260 J/g = 540 cal/g

Enthalpy: for a system at pressure P , adding pressure-volume work onto U

$$H \equiv U + PV$$

$$\begin{aligned} H + \Delta H &= (U + \Delta U) + P(V + \Delta V) && \text{(constant } P) \\ &= (U + PV) + (\Delta U + P\Delta V) \\ &= H + (\Delta U + P\Delta V) \end{aligned}$$

ΔH can come from
either energy increase, or system expansion

Now using 1st law of thermodynamics,

$$\begin{aligned}\Delta U &= Q - P\Delta V + W_{\text{other}}, \\ H &= Q + W_{\text{other}}. \quad (\text{constant } P)\end{aligned}$$

The change in enthalpy is caused only by heat, and other forms of work, *not by pressure-volume work*.

→ If no other types of work are done,
the change in enthalpy tells directly how much heat has been added to the system.

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

Some examples (phase transformation, chemical reaction, ionization, dissolution)

- ΔH when one mole of water boils at 1atm: 40,660 J. (or (40,660 J)/18 g = 2260 J/g)

among 2260 J, some energy is used as the work needed to push the environment away

$$PV = RT = (8.31\text{J/K})(373\text{K}) = 3100\text{J}.$$

- ΔH in the chemical reaction to make liquid water (enthalpy of formation of water): -286 kJ.

In burning 1 mole of H_2 , most (not everything) of -286 kJ is the heat that gets out.

