Phys 344.

Lecture 5. Ref. 1.5, 1.6.

- Quasistatic <u>Adiabatic</u> Compression of an Ideal Gas

$\llcorner\ Q = 0$. — well insulated

— OR fast enough for $Q \approx 0$

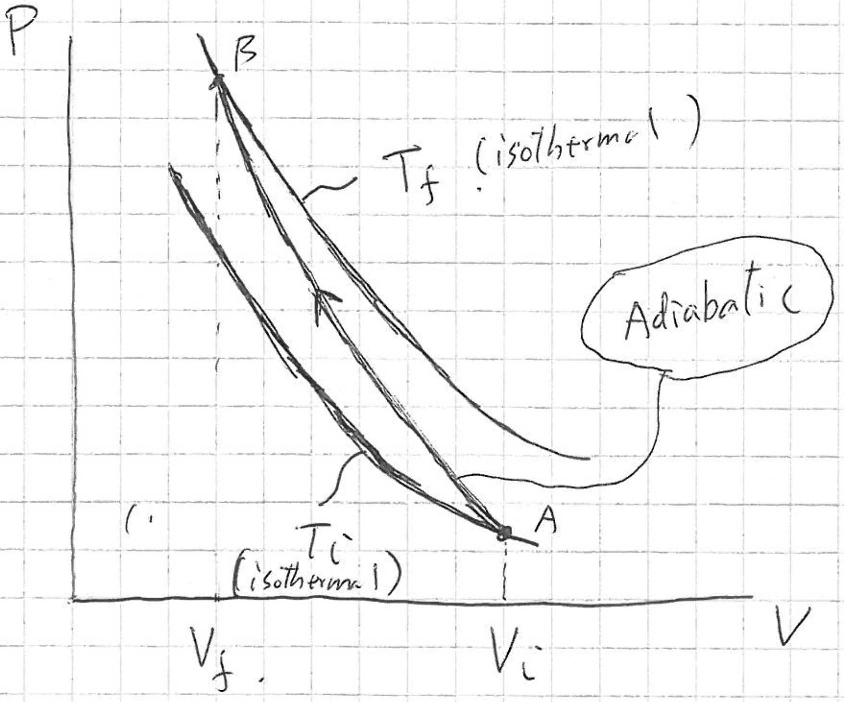
but slow enough for equilibrium.

1st Law:

$$\Delta U = W.$$

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

$$T_f > T_i.$$



For an infinitesmal step:

$$dU = \text{đ}W.$$

$$dU = \frac{f}{2} Nk\,dT.$$

$$\text{đ}W = -P\,dV$$

$$\therefore \quad \frac{f}{2} Nk\,dT = -P\,dV.$$

Since: $NkT = PV$. $\quad Nk\,dT = P\,dV + V\,dP$.

$$\frac{f}{2} P\,dV + \frac{f}{2} V\,dP = -P\,dV, \quad f P\,dV + f V\,dP = -2P\,dV$$

$$fV\,dP = -(2+f)P\,dV.$$

$$\frac{dP}{P} = -\left(\frac{2+f}{f}\right)\frac{dV}{V}.$$

$$\ln\frac{P_f}{P_i} = -\left(\frac{2+f}{f}\right)\ln\frac{V_f}{V_i}.$$

$$\frac{P_f}{P_i} = \left(\frac{V_f}{V_i}\right)^{-\frac{2+f}{f}} = \left(\frac{V_i}{V_f}\right)^{\frac{2+f}{f}} \equiv \left(\frac{V_i}{V_f}\right)^{\gamma}.$$

$$\gamma = \frac{2+f}{f}.$$

$$P_f V_f^{\gamma} = P_i V_i^{\gamma}$$ (for any i and f states along the adiabatic path).

$\therefore$ PV^{γ} = constant.

γ — adiabatic exponent. $\left(\gamma = \frac{2+f}{f}\right)$.

e.g.: diatomic gas at room temperature: $f=5$.

$$\gamma = \frac{2+5}{5} = 1.4$$

Note: ① Adiabatic can be non-quasistatic.

② In quantum mechanics, adiabatic means quasistatic, i.e., SLOW!

- Heat Capacity : $C = \dfrac{Q}{\Delta T}$ (Heat needed for raising 1K)

Specific heat : $c = \dfrac{C}{m}$ (per unit mass)

- However, Q depends on path !

  i.e. difference process leads to different C !

- Heat capacity at <u>constant volume</u>

$$dV = 0,$$
$$W = 0 \quad \text{— No mechanical work}$$
$$Q = \Delta U$$

$$\boxed{C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \nwarrow \text{fix } V.}$$

Note, it's actually the energy needed, when V is fixed, to raise the temperature by 1 K ← (energy can be added by heat or other forms of work)

e.g: use a Microwave oven to heat a cup of water. }

$Q = 0$.

$dV = 0$ (fixed Volume).

but $W \neq 0$. (electric work).

$\Delta U = W$.

"energy" capacity" would be a better name.

- For an ideal gas, $U = \frac{1}{2} N f k T$.

$$= \frac{1}{2} f n R T.$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = \frac{1}{2} N f k = \frac{1}{2} f n R.$$

(Graph on p. 30).

- Heat capacity at constant pressure. $\left(\begin{aligned} \bar{d}Q &= dU - \bar{d}W \\ &= dU + P dV \end{aligned} \right)$.

$$C_P = \left(\frac{\bar{d}Q}{dT}\right)_{\text{fix. } P} = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

(Meaning: $\bar{d}Q$ needs to increase U as well as to drive the expansion work; for ΔT.)

- For an ideal gas: $U = \frac{f}{2} n R T$, $V = \frac{nRT}{P}$.

$$\left(\frac{\partial U}{\partial T}\right)_P = \frac{dU}{dT} = \frac{f}{2} n R = C_V.$$

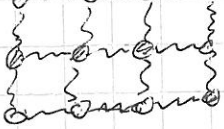
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}, \quad P\left(\frac{\partial V}{\partial T}\right)_P = nR.$$

$$\therefore \quad C_P = C_V + nR = \left(\frac{f}{2} + 1\right) n R.$$

$$C_P / C_V = \frac{\left(\frac{f}{2} + 1\right) \cdot nR}{\frac{f}{2}} = \frac{f+2}{f} = \underset{\substack{\uparrow \\ \text{adiabatic exponent}}}{\gamma}.$$

- For solids, $\left(\frac{\partial V}{\partial T}\right)_P$ usually is small.

$$C_P \approx C_V.$$



since $f = 6$. (vibrations

$$U = \frac{f}{2} NkT = 3NkT = 3nRT.$$

$$C_P \approx C_V = \left(\frac{\partial U}{\partial T}\right) = 3nR.$$

Graphs on page. 30.

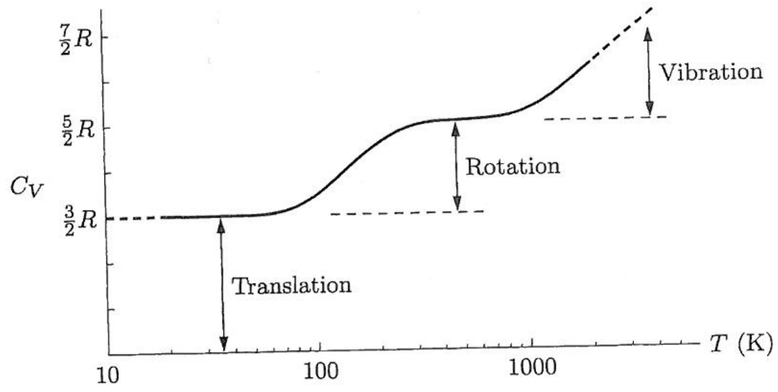


Figure 1.13. Heat capacity at constant volume of one mole of hydrogen (H_2) gas. Note that the temperature scale is logarithmic. Below about 100 K only the three translational degrees of freedom are active. Around room temperature the two rotational degrees of freedom are active as well. Above 1000 K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

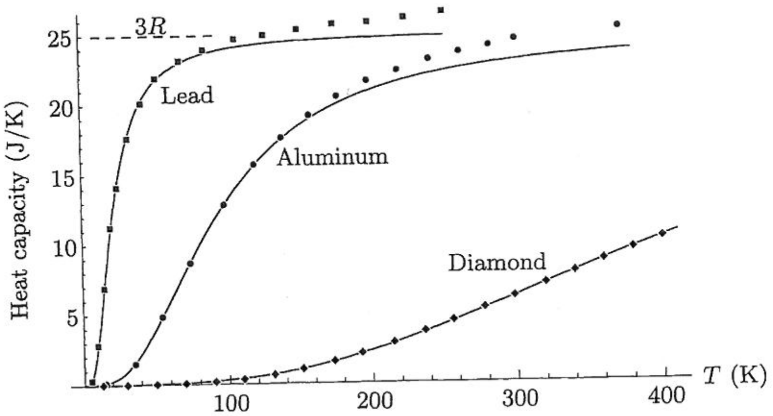


Figure 1.14. Measured heat capacities at constant pressure (data points) for one mole each of three different elemental solids. The solid curves show the heat capacity at constant *volume* predicted by the model used in Section 7.5, with the horizontal scale chosen to best fit the data for each substance.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

Therefore,

$$C_P = C_V + Nk = C_V + nR \qquad \text{(ideal gas)}. \tag{1.48}$$

In other words, for each mole of an ideal gas, the heat capacity at constant pressure exceeds the heat capacity at constant volume by R, the gas constant. Oddly, the

- Latent Heat.

— Required for phase transition
(without changing temperature)

$$L = \frac{Q}{m}.$$

Data in handbooks: usually at $P = 1$ atm. = constant.

e.g.: melting ice: $L = 333$ J/g.

boiling water: $L = 2260$ J/g.
(vapourize)

- Enthalpy.

$$H = U + PV$$

A state quantity, like energy, that is convenient when dealing with heat in a <u>constant-pressure</u> process.

very common, basically anything occurs in the open air ($P = P_{at} = $ const.

e.g. chemical reaction.
phase transition.

- Textbook (Shroeder)'s interpretation. (Cartoon on p. 33)

$$H = \underset{\substack{\uparrow \\ \text{Total energy} \\ \text{of system}}}{U} + \underset{\substack{\uparrow \\ \text{work done} \\ \text{to make room for the system}}}{PV}.$$

∴ H — Energy needed to create the system and put it into the environment (P).

besides the usual constant-pressure expansion or compression. The latent heat for melting ice is 333 J/g, or 80 cal/g. The latent heat for boiling water is 2260 J/g, or 540 cal/g. (To get a feel for these numbers, recall that raising the temperature of water from 0°C to 100°C requires 100 cal/g.)

Problem 1.47. Your 200-g cup of tea is boiling-hot. About how much ice should you add to bring it down to a comfortable sipping temperature of 65°C? (Assume that the ice is initially at −15°C. The specific heat capacity of ice is 0.5 cal/g·°C.)

Problem 1.48. When spring finally arrives in the mountains, the snow pack may be two meters deep, composed of 50% ice and 50% air. Direct sunlight provides about 1000 watts/m^2 to earth's surface, but the snow might reflect 90% of this energy. Estimate how many weeks the snow pack should last, if direct solar radiation is the only source of energy.

Enthalpy

Constant-pressure processes occur quite often, both in the natural world and in the laboratory. Keeping track of the compression-expansion work done during these processes gets to be a pain after a while, but there is a convenient trick that makes it a bit easier. Instead of always talking about the *energy* content of a system, we can agree to always add in the work needed to make room for it (under a constant pressure, usually 1 atm). This work is PV, the pressure of the environment times the total volume of the system (that is, the total space you would need to clear out to make room for it). Adding PV onto the energy gives a quantity called the **enthalpy**, denoted H:

$$H \equiv U + PV. \tag{1.51}$$

This is the *total* energy you would have to come up with, to create the system out of nothing and put it into this environment (see Figure 1.15). Or, put another way, if you could somehow annihilate the system, the energy you could extract is not just U, but also the work (PV) done by the atmosphere as it collapses to fill the vacuum left behind.

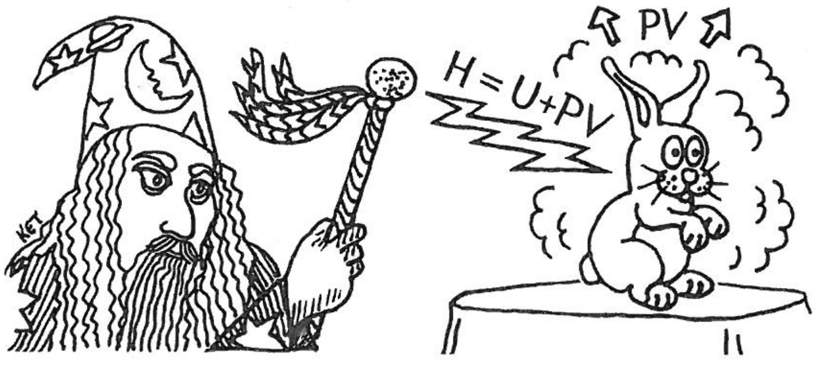


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.