Lecture # 3

Heat capacity, Latent heat, Enthalpy

$$dU = dQ - dW \qquad\qquad dW = PdV$$

$$dU = dQ - PdV$$

(1) $\quad C = dQ/dT$ definition of the heat capacity.

$c = C/m$ - specific heat capacity, (sometimes a term "specific heat" is also used)

$c = C/v$ - molar heat capacity

Another way to write it

$\qquad dT = (1/C)\,dQ$ – we added some heat to a system and measured the change in temperature. The coefficient between two is inverse of heat capacity. Eq. (1) is ambiguous definition. Temperature change depends on whether a system did any work on surroundings. We distinguish two processes: $V = const$ and $P = const$.

$\underline{V = const\ (\ dV = 0)}$

$dU = dQ - dW = dQ - PdV = dQ$

$$C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v \quad \text{For ideal gas, } U = \frac{1}{2}fk_B NT \quad C_V = \frac{1}{2}fk_B N \;.$$

Heat capacity of constant pressure

$$c_p = \left(\frac{dQ}{dT}\right)_P = \left(\frac{dU + PdV}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$\underline{\text{for ideal gas}} \quad U = \frac{1}{2}fk_B NT$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{2}fNk_B$$

$$P\left(\frac{\partial V}{\partial T}\right)_P -? \quad PV = NkT \qquad V = NkT/P$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = P\frac{Nk}{P} = Nk$$

$$c_P = \frac{1}{2}Nkf + Nk$$

$$\frac{c_P}{c_V} = \frac{\frac{1}{2}f + 1}{\frac{1}{2}f} = \frac{f+2}{f} = \gamma \quad \text{adiabatic exponent}$$

From measurements of heat capacity one may determine how many degree of freedom a molecule has and how many degree of freedom in this molecule are 'frozen out' at given temperature.
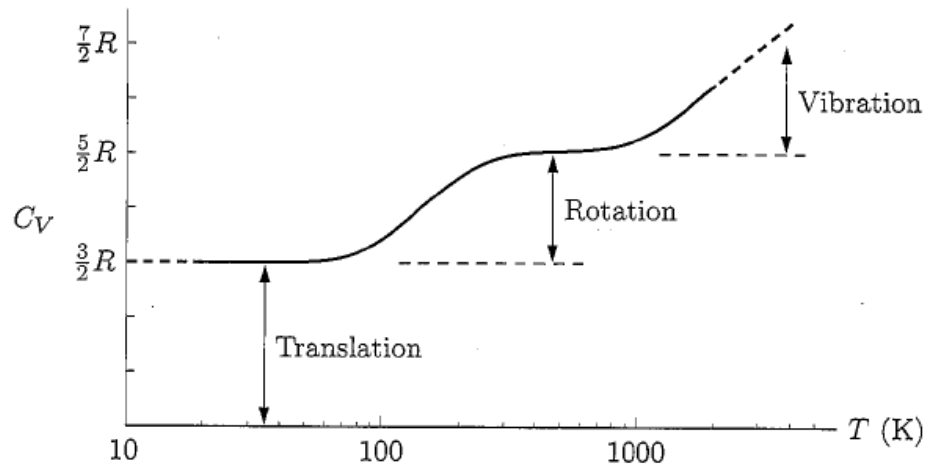
C/m – Specific heat capacity (definition)

C/n - mole heat capacity (definition)

$C_V = \frac{1}{2} fR$ – C_v per mole for ideal gas.

Experimental data

Mole heat capacity of H_2 molecules at V = const as a function of temperature.

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).

Deviations appear because of <u>quantization</u>:
(1) We do not have any problem with translation because momentum may take any number. From uncertainty relation $\Delta p \Delta x \leq h/2\pi$ if Δx is large, Δp can take arbitrary small value.
(2) Rotation Δx is limited by the size of a molecule. Rotational d.o.f. are quantized, i.e. take discreet values recall Bohr model of H atom.
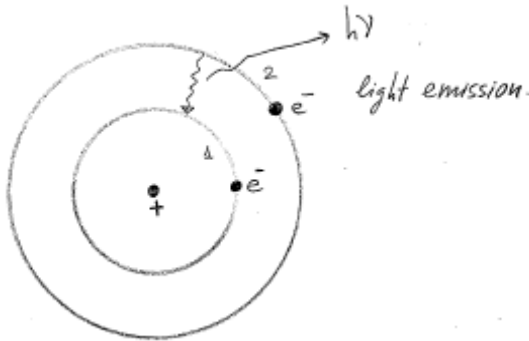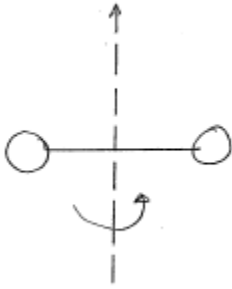

$L = 0, h/2\pi, 2\,h/2\pi, 3\,h/2\pi.$

L-is an angular momentum of an electron rotating around a nucleus.

Let's apply similar rule to the rotation of H_2 molecule.

$M = 1.66. \ 10^{-27} kg = 10^{-3} \ kg/N_a$

$d = 0.7 \ A^° = 7.10^{-11} m$

Lowest excited level $L = h/2\pi$ - quantisation rule.

$h/2\pi = L = I\omega$, where I is a moment of inertia and w is an angular velocity

$I = \sum m_i R_i^2 = 2mR_i^2 = \dfrac{m}{2}d^2$, where d is distance between atoms.

$E = \dfrac{1}{2}I\omega^2 = \dfrac{1}{2}I\left(\dfrac{h/2\pi}{I}\right)^2 = \dfrac{1}{2}\dfrac{(h/2\pi)^2}{I}$ (Lowest possible energy of rotation).
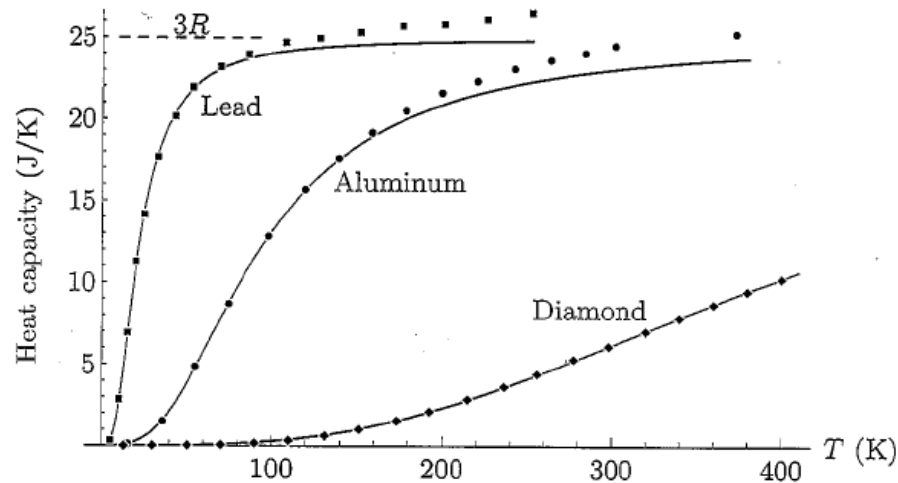
$E = \dfrac{1}{2}\dfrac{(1.05)^2 . 10^{-68} \ J^2.s^2}{1.66.10^{-27} kg.\dfrac{1}{2}(7.10^{-11})^2 m^2} = 1.22.10^{-21} J$

Corresponding effective temperature (at which rotation d.o.f start to 'warm up' and be active).

$E = k_B T$ $T = \dfrac{1.22.10^{-21}}{1.38.10^{-23}} = 88 \ K$

Very closed to experimental temperature where rotational degree of freedom start to appear.

3) Vibrational modes – no easy way to estimate when they are active.

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).

Latent heat

When phase transition takes place heat is taken by the system but temperature does not change. Example: mixture of ice and water.
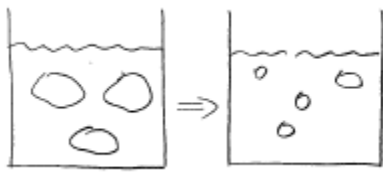
$T_1 = T_2 = 0^0 C$

$L = Q/m$ – latent heat (definition) heat needed to transform 1 kg of substance (usually at p = 1 atm).

Enthalpy

Let us introduce new function (one of the example of the thermodynamic potentials).

$H = U + PV$ - enthalpy

$dH = dU + PdV + VdP$

if $P = $ const $dP = 0.$ then

$dH = dU + PdV$ compare with first law, $dU = dQ - PdV$

$dH = (dQ)_p$

If pressure is kept constant then the charge in the enthalpy is equal to the heat added (subtracted) to (from) the system. Enthalpy is most useful when we are dealing with chemical reaction since most of chemical experiments and technological processes are done ambient pressure condition.
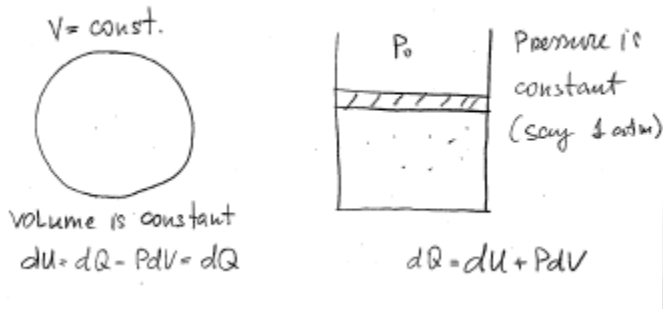
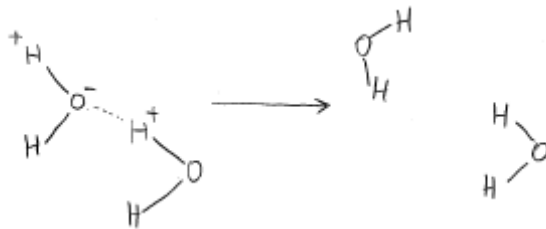$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Example:

1) Boiling water

The heat supplied to the system was spent to

a) Breaking hydrogen bonds (Energy Part)

b) Push away the piston work on environment.

40,66 kJ – change in enthalpy upon boiling 1 mole of water. (Number is from the textbook).

Enthalpy of formation

(How to deal with chemical tables, for example the one you have in the back of your book)

	$\Delta_f H$ (kJ)	C_p (J/K)	1 mole, 298 K, 1 atm
H_2 (g)	0 (standard state)	28.82	
O_2 (g)	0 (standard state)	29.38.	
H_2O (l)	- 285.83	75.29	
H_2O (g)	- 241.82	33.58	

$\Delta H = \Delta_f H_{GAS} - \Delta_f H_{LIQUID} = 44.01$ kJ . The enthalpy difference at 298 K.

To find the enthalpy difference at 100 °C, we perform the following computation

$$\Delta H \,(at\,100^0 c) \approx \Delta H \,(Room.T) + (373 - 298)(K).(C_p(gas) - C_p(liquid)) =$$
$$= 44.01 kJ - 3.13 kJ = 40.88 \, kJ$$

The difference between our estimate and the text book value 40.66 kJ occurs because C_p is slightly temperature dependent.

PROBLEM 1.50 (a) Find ΔH for reaction.

CH_4 (gas) $+2O_2$ (gas) $\rightarrow CO_2$ (gas) $+2H_2O$ (gas)
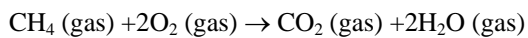
$$\Delta H = (\sum \Delta_f H(products) - (\sum \Delta_f H(reagents)) =$$
$$-393.51 - 2 \times 241.820 - (-74.81) + 2 \times (0) = -802.34 \text{ kJ}$$

The enthalpy of the system decreases by $\Delta H = -802.3 kJ$. So the released heat $+ 802.3$ kJ.