Chapter 5 Statistical Thermodynamics

1. Introduction:
   * Classical thermodynamics:
     ① Macroscopic functions
     ② 2nd law is only a direct result of the fact that has failed to invent a perpetual motion machine (PMM).
       〝Law〞 ⇔ It has not yet been disproved.
   * Physical significance or quantity of S?

2. Entropy and disorder on an atomic scale
   * Gibbs: entropy ⇔ degree of mixed-up-ness at atomic or molecular level.

   e.g. $\begin{cases} \text{solid : more ordered arrangement} \\ \text{liquid : disordered} \\ \text{gas : disordered and random motion} \end{cases}$

   $\therefore S_{(solid)} < S_{(liquid)} < S_{(gas)}$

   EX 1:

   Melting $\qquad$ Solid $\xrightarrow{T_m}$ Liquid $\qquad$ const. T_m, P

   $$\Delta S_m = \frac{\Delta H_m}{T_m} \qquad \because q = \Delta H_m > 0$$

   $$\therefore \Delta S_m \uparrow$$

   Solidification $\qquad$ Liquid $\xrightarrow{T_s}$ Solid $\qquad \Delta S_{(sub)} < 0$

   $\qquad\qquad\qquad\qquad\qquad$ however $\quad \Delta S_{(reservoir)} > 0$

   $\qquad\qquad\qquad\qquad\qquad$ and $\qquad \Delta S_{(tot)} > 0$

   Equilibrium $\qquad$ Solid $\xleftrightarrow{T_m}$ Liquid
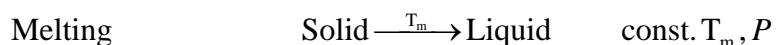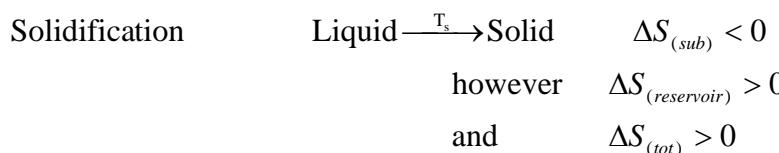
   (no change in disorder) $\Delta S_{tot} = 0$ $\quad$ at T_m $\quad$ (reversible)

   EX 2:

   Supercooled liquid $\xrightarrow[T<T_m]{}$ solid $\qquad\qquad$ (spontaneous)
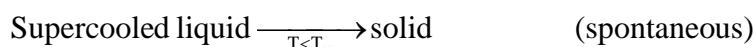
   $\begin{cases} \Delta S_{(sub)} < 0 \\ \Delta S_{(reservoir)} > 0 \end{cases}$

   $\Delta S_{tot} > 0 \qquad\qquad$ irreversible

3. Microstate and macrostate
   * Statistical mechanics: probability
   equil. state ⇔ must probable state.

* Quantum theory: ① quantized energy levels

② $V \uparrow \Leftrightarrow$ (energy gap) $\downarrow$

<u>EX :</u>   4 energy levels: $\varepsilon_0, \varepsilon_1, \varepsilon_2, \varepsilon_3$

3 distinguishable sites: A, B, C

3 indistinguishable atoms

Total U = 3u (macrostate)

Possible microstates? (10)

① possible energy combinations: 3

(a)   (b)   (c)
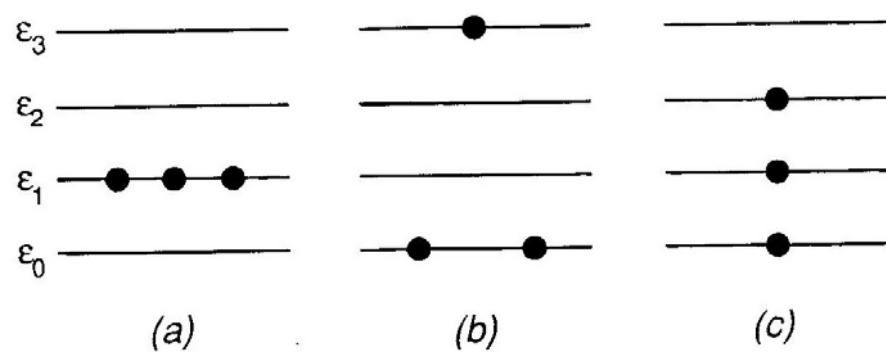
② possible microstates = 10
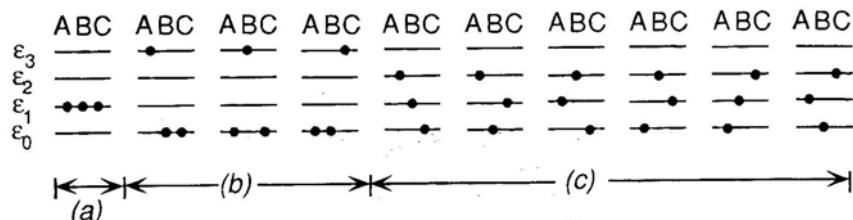
$$\begin{cases} \text{probability of (a)} = \dfrac{1}{10} \\[2mm] \text{probability of (b)} = \dfrac{3}{10} \\[2mm] \text{probability of (c)} = \dfrac{6}{10} \Rightarrow \text{most probable; most mixed - up - ness} \end{cases}$$

4. Determination of the most probable microstate

    * n particles, constant U, V (isolated system)

    * V fixed. => energy levels are fixed

          energy levels: $\varepsilon_0, \varepsilon_1, \varepsilon_{2, \dots\dots\dots}, \varepsilon_r$ (r+1) levels

    $\therefore$ number of arrangements: Ω

$$\therefore \Omega = C(n, n_0) \times C(n - n_0, n_1) \times C(n - n_0 - n_1, n_2) \times \ldots\ldots\ldots \times 1$$

$$= \frac{n!}{n_0!(n - n_0)!} \times \frac{(n - n_0)!}{n_1!(n - n_0 - n_1)!} \times \ldots\ldots\ldots \times 1$$

$$\therefore \Omega = \frac{n!}{n_0! n_1! \ldots\ldots\ldots n_r!} = \frac{n!}{\prod\limits_{i=0}^{r} n_i!}$$

Problem: Determine values of n_i (n_o, n_1, n_2, ..., n_r)
which maximizes Ω.

Stirling's approximation: $\boxed{\ln X! = X \ln X - X}$

$$\therefore \ln \Omega = (n \ln n - n) - \sum\limits_{i=0}^{r}(n_i \ln n_i - n_i)$$

$$\begin{cases} U = cons \tan t = n_0 \varepsilon_0 + n_1 \varepsilon_1 + \ldots.. + n_r \varepsilon_r = \sum\limits_{i=0}^{r} n_i \varepsilon_i \\[3mm] n = cons \tan t = n_0 + n_1 + \ldots.. + n_r = \sum\limits_{i=0}^{r} n_i \end{cases}$$

$$\therefore \quad \delta U = \sum \varepsilon_i \delta n_i = 0 \ldots\ldots\ldots\ldots(1)$$

$$\delta n = \sum \delta n_i = 0 \ldots\ldots\ldots\ldots\ldots(2)$$

$$\delta \ln \Omega = -\sum \left(\delta n_i - \ln n_i + n_i \frac{\delta n_i}{n_i} - \delta n_i \right) = -\sum (\delta n_i \cdot \ln n_i)$$

when $\Omega = \Omega_{\max}$ $\qquad\qquad\qquad$ $\delta \ln \Omega = 0$

$$\therefore \sum (\delta n_i \cdot \ln n_i) = 0 \ldots\ldots\ldots\ldots(3)$$

$(1), (2), (3)$ must be simultaneously satisfied.

Solving method : Lagrange undetermined multipliers : α, β

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ constants.

$\qquad$ (1) : $\quad \sum \beta \varepsilon_i \delta n_i = 0$ $\qquad\qquad\qquad \left(\beta \text{ has unit} : \dfrac{1}{\text{energy}} \right)$

$\qquad$ (2) : $\quad \sum \alpha \cdot \delta n_i = 0$ $\qquad\qquad (\alpha : \text{dimensionless})$

$\qquad \therefore \sum (\ln n_i + \alpha + \beta \varepsilon_i) \cdot \delta n_i = 0$

$(\ln n_0 + \alpha + \beta \varepsilon_0) \cdot \delta n_0 + (\ln n_1 + \alpha + \beta \varepsilon_1) \cdot \delta n_1 + \ldots.. = 0$

Since, $\delta n_i \neq 0$, $\qquad\qquad \therefore \ln n_0 + \alpha + \beta \varepsilon_0 = 0$

$\qquad\qquad\qquad\qquad\qquad\qquad \ln n_1 + \alpha + \beta \varepsilon_1 = 0$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \vdots$

$\therefore \ln n_i + \alpha + \beta \varepsilon_i = 0$

$$\therefore \boxed{n_i = e^{-\alpha} \cdot e^{-\beta \varepsilon_i}}$$

$$n = \sum n_i = \sum e^{-\alpha} \cdot e^{-\beta \varepsilon_i} = e^{-\alpha} \cdot \sum e^{-\beta \varepsilon_i}$$

Define: partition function $\boxed{P \equiv \sum e^{-\beta \varepsilon_i}}$

$$\therefore e^{-\alpha} = \frac{n}{P} \qquad \text{or} \quad \alpha = \ln\left(\frac{P}{n}\right)$$

$$\boxed{n_i = \frac{n}{P} e^{-\beta \varepsilon_i}}$$

When n is very large, $\Omega_{max} \sim \Omega_{tot}$

$$\therefore \ln \Omega_{tot} \cong \ln \Omega_{max} = (n \ln n - n) - \sum (n_i \ln n_i - n_i) = n \ln n - \sum n_i \ln n_i$$

$$= n \ln n - \sum \left(\frac{n}{P} \cdot e^{-\beta \varepsilon_i}\right) \cdot \ln\left(\frac{n}{P} \cdot e^{-\beta \varepsilon_i}\right)$$

$$= n \ln n - \frac{n}{P} \sum e^{-\beta \varepsilon_i} \cdot (\ln n - \ln P - \beta \varepsilon_i)$$

$$= n \ln n - \frac{n}{P}(\ln n - \ln P) \cdot \sum e^{-\beta \varepsilon_i} + \frac{n\beta}{P} \sum \varepsilon_i \cdot e^{-\beta \varepsilon_i}$$

$$\because U = \sum n_i \varepsilon_i = \sum \frac{n}{P} \varepsilon_i \cdot e^{-\beta \varepsilon_i} = \frac{n}{P} \sum \varepsilon_i \cdot e^{-\beta \varepsilon_i}$$

$$\therefore \ln \Omega_{tot} = n \ln P + \beta U \dots\dots(1)$$

$$\therefore \frac{1}{\beta} \delta \ln \Omega_{tot} = \delta U \dots\dots(2)$$

c.p. at constant V, $dU_V = TdS$

Boltzmann equation: $\boxed{S \equiv k \ln \Omega}$

$$\therefore dS = k \cdot d \ln \Omega$$
$$TdS = kT \cdot d \ln \Omega$$
$$TdS = kT \cdot d \ln \Omega = dU_V \dots(3)$$

$$\therefore \boxed{\beta = \frac{1}{kT}} \qquad \boxed{P = \sum e^{-\frac{\varepsilon_i}{kT}}}$$

$$\therefore \boxed{\frac{n_i}{n} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{P}}$$

<u>Note:</u>

$*$ $\because S \equiv k \ln \Omega$

$\therefore$ Equilibrium at constant U, V, n is that $S = S_{max}$, therefore, $\Omega = \Omega_{max}$.

$*$ $\because \dfrac{n_i}{n} = \dfrac{e^{-\frac{\varepsilon_i}{kT}}}{P}$ $\therefore T \uparrow \Rightarrow n_i \uparrow$ at higher ε_i, $n_i \downarrow$ at lower ε_i
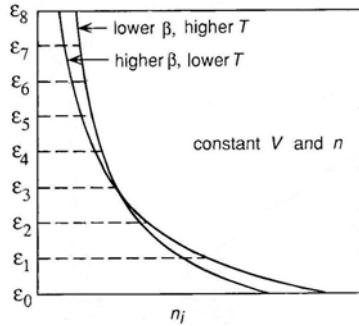

$\dfrac{n_{10}}{n_1} = e^{-\frac{1}{kT}(\varepsilon_{10} - \varepsilon_1)} = e^{-\frac{\Delta\varepsilon}{kT}}$

$\because \Delta\varepsilon > 0, \ \therefore T \uparrow \Rightarrow \left(\dfrac{n_{10}}{n_1}\right) \uparrow$

5. Heat flow and entropy production

* Irreversible process: production of entropy.

<u>EX:</u> T_A $>$ T_B

Ω_A Ω_B $\Omega_A \cdot \Omega_B$
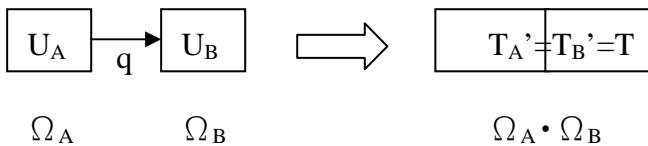
$\Omega'_A(U_A')$ $\Omega'_B(U_B')$

$\Delta\Omega_A$ < $\Delta\Omega_B$ equil. $(\Omega_A \Omega_B)_{max}$

$\therefore$ $\delta \ln(\Omega_A \Omega_B) = 0$ at equil.   (Reversible)
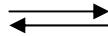
From (2) in previous page: $\delta \ln \Omega = \dfrac{\delta U_V}{kT} = \dfrac{\delta Q}{kT}$ (For constant V)

$\therefore$ For spontaneous irreversible process: $\delta \ln(\Omega_A \Omega_B) > 0$

$\delta \ln \Omega_A = \dfrac{\delta Q_A}{kT_A}$

$\delta \ln \Omega_B = \dfrac{\delta Q_B}{kT_B}$

$\delta Q_A = -\delta Q_B = \delta q < 0$ $(T_A > T_B)$

$\therefore \delta \ln \Omega_A \Omega_B = \delta \ln \Omega_A + \delta \ln \Omega_B$

$\qquad = \left(\dfrac{1}{T_A} - \dfrac{1}{T_B}\right)\dfrac{\delta Q}{k} > 0$

6. Configurational entropy and thermal entropy

    * Thermal entropy: redistribution of particles in energy levels during heat transfer

        S_{th} (thermal energy).

    * Configurational entropy: distribution of particles in space.

        $S_{conf.}$

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$$\begin{cases} \Omega_{4:0} = 1 \\ \Omega_{3:1} = 16 \quad C(4,3) \times C(4,1) \\ \Omega_{2:2} = 36 \quad C(4,2) \times C(4,2) \quad \text{Total} = C(8,4) = \dfrac{8!}{4!4!} = 70 \\ \Omega_{1:3} = 16 \quad C(4,1) \times C(4,3) \\ \Omega_{0:4} = 1 \end{cases}$$

        $\therefore$ 2:2 is the most probable state $\Longleftrightarrow$ most random

        $S \equiv k \ln \Omega$, $S = S_{max}$

  EX:

    | A | B | | A+B | mixing

    State (1)   State (2)
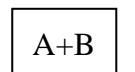
$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1 = k \ln \left(\frac{\Omega_2}{\Omega_1} \right)$$

$$\Omega_1 = 1, \quad \Omega_2 = \frac{(n_a + n_b)!}{n_a! n_b!}, \qquad \therefore \Delta S = k \ln \left[\frac{(n_a + n_b)!}{n_a! n_b!} \right]$$

* $\boxed{S_{total} = S_{th} + S_{conf.}}$

        $= k \ln \Omega_{th} + k \ln \Omega_{conf.}$

        $= k \ln \Omega_{th} \Omega_{conf.}$

        $\therefore \Delta S_{tot} = k \ln \dfrac{\Omega_{th(2)} \cdot \Omega_{conf.(2)}}{\Omega_{th(1)} \cdot \Omega_{conf.(1)}}$

$$\begin{cases} \text{(1) For mixing at constant T:} \quad \Delta S_{tot} = k \ln \dfrac{\Omega_{conf.(2)}}{\Omega_{conf.(1)}} \\[4mm] \text{(2) Heat transfer only:} \quad \Delta S_{tot} = k \ln \dfrac{\Omega_{th(2)}}{\Omega_{th(1)}} \end{cases}$$

    * Ideal mixing: mixing does not cause a redistribution of particles among energy

      levels. i.e., $\Omega_{th(2)} = \Omega_{th(1)}$, (complete randomness)

    Usually, $\Omega_{th(2)} \neq \Omega_{th(1)}$,

          Clustering or ordering may occur.

$4 = (2A+2B)$ random

$> 2A$ clustering

$< 2B$ ordering
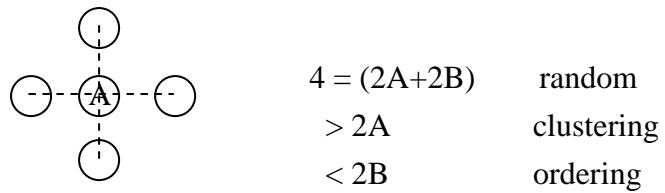
EX1: Spectroscopic examination of excited N_2 molecules:

$$\varepsilon_i = (i + 1/2)h\nu \qquad \begin{cases} \upsilon = 7 \times 10^{13}\, s^{-1} \\ h = 6.6252 \times 10^{-34}\, J \cdot s \end{cases}$$

$$\begin{cases} i & 0 & 1 & 2 & 3 \\[2mm] \dfrac{n_i}{n_o} & 1.00 & 0.250 & 0.062 & 0.016 \end{cases}$$

$$\begin{cases} (1) \text{ Proof of equilibrium distribution} \\ (2)\ T = ? \end{cases}$$

Solu: (1) At equilibrium.

$$\frac{n_i}{n} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{P} = \frac{\exp\left[-\left(i + \dfrac{1}{2}\right)\dfrac{h\upsilon}{kT}\right]}{P}$$

$$\therefore \frac{n_1}{n_o} = \frac{\exp\left(-\dfrac{3}{2}\dfrac{h\upsilon}{kT}\right)}{\exp\left(-\dfrac{1}{2}\dfrac{h\upsilon}{kT}\right)} = \exp\left(-\frac{h\upsilon}{kT}\right) = 0.250$$

$$\therefore \frac{h\upsilon}{kT} = 1.386$$

$$\therefore T = \frac{h\upsilon}{1.386k} = \frac{6.6252 \times 10^{-34} \times 7 \times 10^{13}}{1.386 \times \left(1.38 \times 10^{-23}\right)} = 2420K.$$

(2) $\because P \cdot \dfrac{n_o}{n} = \exp\left(-\dfrac{1}{2}\dfrac{h\upsilon}{kT}\right) = 0.5$

$P \cdot \dfrac{n_1}{n} = \exp\left(-\dfrac{3}{2}\dfrac{h\upsilon}{kT}\right) = 0.125$

$P \cdot \dfrac{n_2}{n} = \exp\left(-\dfrac{5}{2}\dfrac{h\upsilon}{kT}\right) = 0.031$ if equil at T = 2420K

$P \cdot \dfrac{n_3}{n} = \exp\left(-\dfrac{7}{2}\dfrac{h\upsilon}{kT}\right) = 0.008$

$$\therefore Normalize: \frac{P\dfrac{n_1}{n}}{P\dfrac{n_o}{n}} = \frac{n_1}{n_o} = \frac{0.125}{0.5} = 0.25$$

$$\frac{P\dfrac{n_2}{n}}{P\dfrac{n_o}{n}} = \frac{n_2}{n_o} = \frac{0.031}{0.5} = 0.062$$

$$\frac{P\dfrac{n_3}{n}}{P\dfrac{n_o}{n}} = \frac{n_3}{n_o} = \frac{0.008}{0.5} = 0.016$$

$\therefore$ Observed distribution is equil.

<u>EX2:</u>   Isotopes of Pb:

M	at%	N
204	1.5	$0.015N_o$
206	23.6	$0.236N_o$
207	22.6	$0.226N_o$
208	52.3	$0.523N_o$

Molar configurational entropy $S_{conf.}$ = ?

<u>Solu:</u>

$\because S = k\ln\Omega$

$$\therefore \Omega = \frac{(N_o)!}{(0.015N_o)!(0.236N_o)!(0.226N_o)!(0.523N_o)!}$$

$$\therefore \ln\Omega = (N_o\ln N_o - N_o) - (0.015N_o\ln 0.015N_o - 0.015N_o)$$
$$- (0.236N_o\ln 0.236N_o - 0.236N_o) - \ldots\ldots\ldots$$
$$= 6.5\times 10^{23}$$

$$\therefore S_{conf.} = k\ln\Omega = (1.38\times 10^{-23})\times(6.5\times 10^{23}) = 8.97 \, {}^{J}\!/\!_{mole \cdot K}$$

7. Calculation of S, A, U, C_v from P

From (1) in page 5-4, $\ln\Omega_{tot} = n\ln P + \beta U$

$$= n\ln P + \frac{U}{kT}$$

$$S = k\ln\Omega_{tot} = nk\ln P + \frac{U}{T} \quad \because A \equiv U - TS = U - T\cdot\left(\frac{U}{T} + nk\ln P\right)$$

$$\therefore A = -nkT\ln P \quad \text{and} \quad dA = -SdT - PdV$$

$$\therefore S = -\left[\frac{\partial A}{\partial T}\right]_V = nk\ln P + nkT\left(\frac{\partial \ln P}{\partial T}\right)_V$$

$$U = A + TS = -nkT \ln P + T\left[nk \ln P + nkT \left(\frac{\partial \ln P}{\partial T} \right)_V \right]$$

$$\therefore U = nkT^2 \left(\frac{\partial \ln P}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 2nkT \left(\frac{\partial \ln P}{\partial T} \right)_V + nkT^2 \left(\frac{\partial^2 \ln P}{\partial T^2} \right)_V$$

* Calculation of V, H, G, C_p requires the volume dependence of partition function.

8. Internal energy
   Heat capacity $\Big\}$ of a crystal.(C_V)
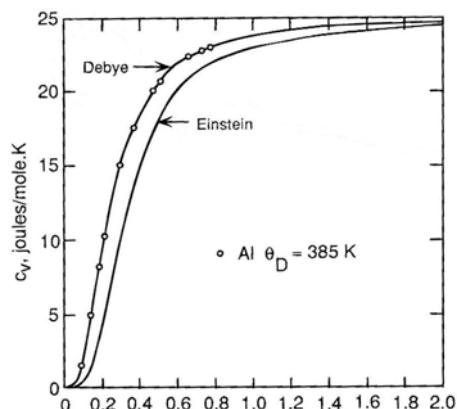
Einstein's model: * Simple cubic structure.
(each atom has 6 nearest neighbors)

* Bonding $\Longleftrightarrow$ Spring

Crystal energy $\Longleftrightarrow$ Oscillators
(Internal energy)

$$\therefore \begin{cases} N_o \text{ atoms} \\ 3N_o \text{ oscillators} \\ (\because \text{each bond is shared by 2 atoms}) \end{cases}$$

Coupled oscillation $\Longrightarrow$ only certain discrete vibrational frequencies can occur.

$\Longrightarrow$ Bond energies are "quantized"

Allowable energy: $\varepsilon_i = (i + 1/2)h\nu$ (i = 0, 1,.....)

h: Plank's const. = 6.624×10^{-27} erg $\cdot$ sec/atom

* characteristic freq. ν is the only adjustable parameter: $\nu = \nu_E$

$\nu \Leftrightarrow$ spring constant.

different solid => different ν

ν can be determined by curve fitting. $C_V(T)$, which is measured experimentally.

$$P = \sum_{i=0}^{r} e^{-\varepsilon_i / kT} = \sum_{i=0}^{r} e^{-\frac{1}{kT}\left(i+\frac{1}{2}\right)h\nu} = e^{-\frac{h\nu}{2kT}} \cdot \sum_{i=0}^{r} e^{-\frac{h\nu}{kT}i}$$

$$\because \sum_{i=0}^{\infty} e^{-ix} \quad \frac{1}{1-e^{-x}}, \qquad x = \frac{h\nu}{kT}$$

let $r = \infty$

$$\therefore P = \frac{e^{-\frac{h\upsilon}{2kT}}}{\left[1 - e^{-h\upsilon/kT}\right]}$$

$$\ln P = -\frac{h\upsilon}{2kT} - \ln\left[1 - e^{-h\upsilon/kT}\right]$$

$$\frac{\partial \ln P}{\partial T} = \frac{h\upsilon}{2kT^2} - \frac{-\frac{h\upsilon}{kT^2} \cdot e^{-h\upsilon/kT}}{\left[1 - e^{-h\upsilon/kT}\right]}$$

$$= \frac{h\upsilon}{2kT^2}\left\{1 + \frac{2e^{-h\upsilon/kT}}{\left[1 - e^{-(h\upsilon/kT)}\right]}\right\}$$

$$= \frac{h\upsilon}{2kT^2} \cdot \frac{\left[1 - e^{-h\upsilon/kT}\right] + 2e^{-h\upsilon/kT}}{1 - e^{-(h\upsilon/kT)}} = \frac{h\upsilon}{2kT^2} \cdot \frac{\left[1 + e^{-h\upsilon/kT}\right]}{\left[1 - e^{-h\upsilon/kT}\right]}$$

$\because 3N_o$ oscillators.

$$3N_o kT\left[\frac{\partial \ln P}{\partial T}\right]_V = U = A + TS = \frac{3}{2}N_o h\upsilon \cdot \frac{\left(1 + e^{-h\upsilon/kT}\right)}{\left[1 - e^{-h\upsilon/kT}\right]}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N_o k\left(\frac{h\upsilon}{kT}\right)^2 \cdot \frac{e^{-\frac{h\upsilon}{kT}}}{\left[1 - e^{-\frac{h\upsilon}{kT}}\right]^2} = 3N_o k \cdot \left(\frac{h\upsilon}{kT}\right)^2 \cdot \frac{e^{\frac{h\upsilon}{kT}}}{\left(e^{h\upsilon/kT} - 1\right)^2}$$

Define : Einstein temperature, $\theta_E \equiv \dfrac{h\upsilon}{k}$ (See Gaskell sec. 6.2 & 6.3)

$$N_o = N_A \qquad \therefore N_o k = R$$

$$\therefore C_V = 3R \cdot \left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{\frac{\theta_E}{T}}}{\left[e^{\theta_E/T} - 1\right]^2},$$

Compare with experimental data, Fig. 6.2 (Al) & Fig. 6.3 (Diamond)
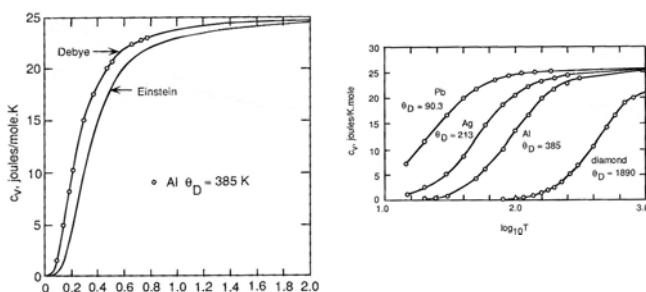

* High T, $C_v \Leftrightarrow 3R$
* C_v(Einstein) -> 0, when T-> 0.
  Faster than experimental data.

$*$ | Dulong – Petit Rule | (1819): $C_v=3R$, all solid elements. (high T)

(Empirical rule, not always correct.)

$*$ Debye theory of C_v

(1) Elastic vibration of a continuous solid.

Frequency spectrum: $g(\upsilon) = \dfrac{9N}{\upsilon_m^{\ 3}} \upsilon^2$
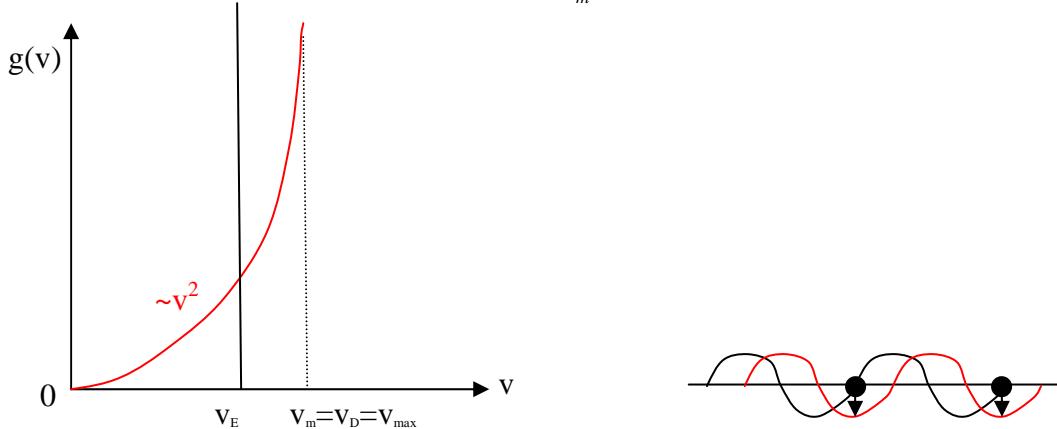
$\int_0^{\upsilon_m} g(\upsilon) \cdot d\upsilon = 3N_o$: total oscillators

$\upsilon_{max} = \dfrac{\upsilon}{\lambda_{min}}$
$\begin{cases} (\lambda_{min} = 2a) & \lambda = na \\ \upsilon : wave\ velocity \end{cases}$

Define $\upsilon_D = \upsilon_m$, $\quad \theta_D = \dfrac{h\upsilon_D}{k}$: Debye Temperature.

$\therefore C_V = 9R\left(\dfrac{T}{\theta_D}\right)^3 \cdot \int_0^{\frac{\theta_D}{T}} \dfrac{x^4 e^{-x}}{(1 - e^{-x})^2} \cdot dx \qquad where \quad x = \dfrac{h\upsilon}{kT}$

At very low temperature. (x $\rightarrow \infty$) $C_v \doteqdot T^3$ (Debye T^3 law)

Debye curve is in very good agreement with experimental data.

$*$ C_v of electrons (see Thermodynamics, Kinetic theory and statistical thermodynamics, by F.W. Sears and G.L. Salinger, §13-6, p 407-413)

Free electron gas,

$$C_V = \dfrac{\pi^2 R}{2}\left(\dfrac{kT}{E_F}\right) = bT \qquad or \qquad C_V \sim T$$

However, contribution of electron to C_v of a metal is very small (low T) compared to atom vibration. Because only very few electrons can be excited to high energies.
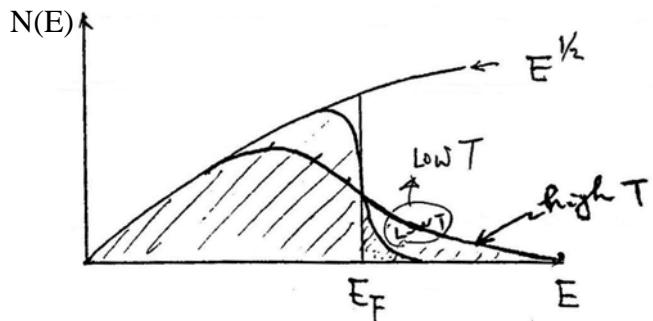
Very high T, C_v becomes important.

$C_p = a + bT + cT^{-2}$

* In view of the discrepancies between theoretical calculated C_v values and experimentally determined value, it is normal practice to experimentally determine $C_p(T)$ of a substance.

   Empirical $C_p = a + bT + c/T^2$

* | Kopp's rule: | $C_p (A_mB_n) = mC_p(A) + nC_p(B)$

   Heat capacity of a solid compound is equal to the sum of heat capacities of its constituent elements.

9. U and C_v of ideal gas

   Monatomic ideal gas model

   Assumption: The energy contributed by each particle is simply the kinetic energy associated with its translation through space.

   Specific 6 variables for each atom: $\begin{cases} position : \vec{r}(x, y, z) \\ velocity : \vec{v}(v_x, v_y, v_z) \end{cases}$

   $$\therefore \varepsilon = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x{}^2 + v_y{}^2 + v_z{}^2\right)$$

   Note: the variables are not quantized. The velocity and the position may vary continuously.

   $\begin{cases} -\infty < v_x(v_y, v_z) < +\infty \\ 0 \le x \le l_x, \ \ 0 \le y \le l_y, \ \ 0 \le z \le l_z \end{cases}$ $\therefore P = \sum_{i=1}^{\infty} e^{-\varepsilon_i / kT}$

   $$\therefore P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\varepsilon/kT} \cdot dv_x dv_y dv_z dxdydz$$

   Note: Position and velocity coordinates are independent of each other.

   $$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dxdydz \cdot \int_{-\infty}^{\infty} e^{-\frac{mv_x{}^2}{2kT}} dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y{}^2}{2kT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z{}^2}{2kT}} dv_z$$

   $$\because v = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dxdydz$$

$$\because \int_{-\infty}^{\infty} e^{-a^2 x^2} \cdot dx = \frac{\sqrt{\pi}}{a} \qquad\qquad \therefore \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2kT}} \cdot dv = \sqrt{\frac{2\pi kT}{m}}$$

$$\therefore P = v \cdot \left(\frac{2\pi kT}{m}\right)^{3/2} \qquad\qquad \therefore \ln P = \ln v + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T$$

$$N_o kT^2 \left(\frac{\partial \ln P}{\partial T}\right)_V = U = A + TS = \frac{3}{2}N_o kT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}N_o k$$

Note : (1) U is a function of T only!

(2) C_V is constant. For $N_o = N_A$ $\quad C_V = \frac{3}{2}N_A k = \frac{3}{2}R$

(3) Proof for $N_A k = R$

$$\because dA = -SdT - PdV + \delta w'$$

$$\therefore P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$\therefore P = N_o kT \cdot \left(\frac{\partial \ln P}{\partial V}\right)_T = N_o kT \cdot \frac{1}{V} \qquad \therefore PV = N_o kT$$

For one mole : $N_o = N_A, \quad PV = N_A kT$

compare with ideal gas law (experiment) : $PV = nRT \quad (n = 1)$

$$\therefore N_A k = R \qquad \text{or} \quad k = \frac{R}{N_A}$$

10. Diatomic ideal gas (Polyatomic gas)

Kinetic energy of a molecule $\begin{cases} \text{Translation of mass center} \\ \text{Rotation} \\ \text{vibratioin of atoms about mass center} \end{cases}$

* Simplification: each component of kinetic energy has the same mathematical form. (e.g. Rotation: $E_k = Iw^2/2$ (v = Rw);

SHM: $E_k = mw^2(A^2-x^2)/2$ (v = dx/dt = wAcos(wt+a)

x = Asin(wt+a))

$$\therefore \varepsilon = \sum_{j=1}^{n} b_j v_j^2 \qquad \text{n: number of independent motion components.}$$

e.g. * one rotation term, if molecule has an axis of symmetry.

* one vibration term for each bond in the molecule structure.

$$\therefore P = \iiint dxdydz \cdot \int_{-\infty}^{\infty}.......\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{1}{kT}\sum_{j=1}^{n} b_j v_j^2} \cdot dv_1 \cdot dv_2.....dv_n$$

$$= V \cdot \iint ....\int_{-\infty}^{\infty} \cdot \left[\prod_{j=1}^{n} e^{-\frac{b_j}{kT}v_j^2}\right] \cdot dv_1 \cdot dv_2......dv_n$$

$$= V \cdot \prod_{j=1}^{n} \left[\int_{-\infty}^{\infty} e^{-\frac{b_j}{kT} v_i^2} \cdot dv_j \right] \qquad \int e^{-a^2 x^2} dx = \frac{\sqrt{\pi}}{a}$$

$$\therefore P = V \cdot \prod_{j=1}^{n} \left(\frac{\pi kT}{b_j} \right)^{1/2}$$

$$\ln P = \ln V + \sum_{j=1}^{n} \frac{1}{2} \ln \left(\frac{\pi k}{b_j} \right) + \sum_{j=1}^{n} \frac{1}{2} \ln T$$

$$U = N_o kT^2 \left(\frac{\partial \ln P}{\partial T} \right)_V = N_o kT^2 \cdot \left(\frac{n}{2T} \right) = n \cdot \frac{1}{2} N_o kT = n \cdot \frac{RT}{2}$$

$$\therefore C_V = \left(\frac{\partial U}{\partial T} \right)_V = n \cdot \frac{1}{2} N_o k = n \cdot \frac{R}{2}$$

* C_v depends on the number of independent components of motion that the molecule can display.

i.e. Each independent component of motion of the molecule in the gas contributes the same quantity, kT/2, to the internal energy.

=> | Principle of equipartion of energy |

* Ar, He, Ne   Cv~3R/2   (3 translation)

H$_2$, O$_2$, N$_2$ Cv~5R/2   (3 translation+1R+1 vib)

NH$_3$ Cv~7R/2   (3 t+1R+3 vib)

* For N$_2$, ∵ bond is stiff

∴ Vibrational E. < Rotational E. < Translation E.