

Kinds of Ensemble :-  $N, V, T, E$ .

- ① Micro Canonical Ensemble -  $N, V, E$  fixed  $T$  varied
- ② Canonical ensemble -  $N, V, T$  fixed  $E$  varied.
- ③ Grand ensemble -  $N, T$  fixed  $N, E$  varied.

Monatomic Ideal gas → Let us consider a monoatomic ideal gas consisting of  $N$  identical particles, each of mass  $m$  enclosed in a container of volume  $V$  at a temp  $T$ . The energy of a molecule may be written as,

$$E = \frac{mv^2}{2m} = \epsilon_K \quad \text{--- ①}$$

where the first term is the kinetic energy of the translational motion and  $\epsilon_K$  is the energy associated with an internal state of the motion.

the partition function of a system in this case is given

$$\text{by, } Q_N = \frac{1}{N!} [Q_1]^N \quad \text{--- ②}$$

where  $Q_1$  is a single particle partition function.

$$Q_1 = Q_{tr} Q_{in} \quad \text{--- ③}$$

$Q_{tr}$  is the translational partition function and is given by

$$Q_{tr} = \frac{1}{h^3} \int_0^\infty \int_0^\infty \int_0^\infty e^{-\frac{h^2}{2mkT}(q_x^2 + q_y^2 + q_z^2)} dq_x dq_y dq_z \\ = V \left[ \frac{2\pi mkT}{h^2} \right]^{3/2} \quad \text{--- ④}$$

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which is the equation of state for an ideal gas.

the entropy of an ideal gas is,

$$S = - \left( \frac{\partial A}{\partial T} \right) \\ = NR \log \left( \frac{V}{N} \right) + \frac{3}{2} NR \log (RT) + \frac{3}{2} NR + \frac{5}{2} NR \log \left( \frac{2\pi m}{h^2} \right) + NR.$$

$$= NR \log \left[ \frac{V}{N} \left( \frac{2\pi m RT}{h^2} \right)^{3/2} \right] + \frac{5}{2} NR.$$

or,  $\frac{S}{R} = N \log \left[ \frac{V}{N} \left( \frac{2\pi m RT}{h^2} \right)^{3/2} \right] + \frac{5}{2} N$  — (10)  
which is known as the Sackur-Tetrode equation.

the energy is,

$$U = A + TS \\ = \frac{3}{2} NRT \quad \text{--- (11)}$$

and finally the specific heat at constant volume is,

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

which is independent of temperature.

The pressure of an ideal gas is  $P = - \left( \frac{\partial A}{\partial V} \right)_{NT}$

$$= \frac{NR}{V}$$

$$\text{or, } P \cdot V = NKT.$$

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Ensemble  $\rightarrow$  Phase space of particle = Configuration space + momentum space.

Volume element in phase space  $= dq dp$ .

$$\langle f \rangle = \int f \cdot \psi^* \psi dq = \int \int f p dq, \langle f \rangle = \int \int f p dq dp \\ = \int dq dp_1, dq_2 dp_2, \dots, dq_n dp_n$$