

Ideal gas of Monoatomic Particles

only translational motion, no rotational or vibrational degrees of freedom

motion of the center of mass.

At low densities, high temperatures, or particles with large mass \Rightarrow classical statistics applies $Q(N, V, T) = (q(V, T))^N / N!$ \Rightarrow no interactions where $q(V, T)$ is single-particle partition function

Note this itself may be summed over quantum states or classical states

For monoatomic particles $q(V, T) = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}}$

These degrees of freedom are independent of each other

q_{trans} , Translational partition function:

Particle in a box of side L .

Allowed energies are given as $\epsilon_{n_x n_y n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$ $n_x, n_y, n_z = 1, 2, \dots$

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \epsilon_{n_x n_y n_z}}$$

$$q_{\text{trans}} = \left(\sum_{n_x=1}^{\infty} e^{-\beta n_x^2 h^2 / 8mL^2} \right) \left(\sum_{n_y=1}^{\infty} e^{-\beta n_y^2 h^2 / 8mL^2} \right) \left(\sum_{n_z=1}^{\infty} e^{-\beta n_z^2 h^2 / 8mL^2} \right)$$

These degrees of freedom are independent

$$q_{\text{trans}} = \left(\sum_{n=1}^{\infty} \exp^{-\beta n^2 h^2 / 8mL^2} \right)^3$$

\hookrightarrow The three directions are identical.

$$q_{\text{trans}}(V, T) = \left(\int_0^{\infty} e^{-\beta h^2 n^2 / 8mL^2} dn \right)^3$$

Thus the discrete sum is replaced by a continuous distribution of energies \therefore At room temperatures typical value of $n_{x/4/2}$ is $0(10^{10}) \therefore h$ is so small.

$$\text{Set } x = nh / \sqrt{8kTmL^2}$$

$$\therefore q_{\text{trans}} = \left(\int_0^{\infty} e^{-x^2} dx \cdot \frac{\sqrt{8kTmL^2}}{h} \right)^3$$

$$q_{\text{trans}} = \left(\frac{8kTm}{h^2} \right)^{3/2} \cdot V \left(\int_0^{\infty} e^{-x^2} dx \right)^3$$

$$q_{\text{trans}} = \left(\frac{8kTm}{h^2} \right)^{3/2} V \left(\frac{\sqrt{\pi}}{2} \right)^3$$

$$q_{\text{trans}} = \left(\frac{2mKT\pi}{h^2} \right)^{3/2} V$$

$\sqrt{\frac{h^2}{2mKT\pi}}$ is λ , the thermal De-Broglie wavelength

$$\therefore q_{\text{trans}} = \frac{V}{\lambda^3}$$

When $\lambda^3 \ll V$, the energy levels can be assumed to have a continuous distribution and q_{trans} is evaluated in the classical limit.

matter wave extent much smaller than size of box, \therefore the particles energy levels can be treated as a classical continuum.

Average Energy of translation for a particle is given by

$$E_{\text{trans}} = - \frac{\partial \ln q_{\text{trans}}}{\partial \beta}$$

$$E_{\text{trans}} = kT^2 \left(\frac{\partial \ln q_{\text{trans}}}{\partial T} \right)$$

$$E_{\text{trans}} = kT^2 \left(\frac{3}{2} \frac{1}{T} \right) = \frac{3}{2} kT$$

For Each one of the degrees of freedom $q_{\text{trans}, x/y/z} = (q_{\text{trans}})^{1/3}$

$$\therefore E_{x/y/z} = \frac{1}{2} kT$$

Thus average energy is $1/2 kT$ per degree of freedom. We'll soon see that this is quite a general result (known as the theorem of equipartition of energy)

electronic & nuclear partition function:

$$q_{\text{elec}} = \sum_i \omega_i e^{-\beta \epsilon_i}$$

ω_i is degeneracy and ϵ_i is energy of i^{th} state.

By setting ϵ_1 arbitrarily to 0, we express q_{elec} in terms of ground state.

energy levels of electronic levels w.r.t. ground level.

$$q_{\text{elec}} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \epsilon_{12}} + \dots$$

$\Delta \epsilon_{ij}$ = energy level of j^{th} level w.r.t. ground level.

Typical $\Delta \epsilon$ is $O(\text{few eV})$. $\beta \Delta \epsilon$ is very large at room temperature. Thus, in most cases only first term counts.

For some atoms (halogens), a few terms count.

(Note the degeneracies of the ^{one-electron or few electron} electronic levels do not increase exponentially as a fun^2 of energy)

would add a ~~constant~~ constant to the average energy. does not contribute to heat capacity or temperature dependence

Nuclear partition function has same form of electronic partition function. However, nuclear energies are of the order of MeVs so nuclei are excited only at temperatures of $0(10^{10} \text{ K})$. So at terrestrial temperatures, nuclei can be assumed to be in their ground state, which is assumed to have zero energy.

only first term w_{n1} counts. The nuclear partition function $q = w_{n1}$ introduces a simple multiplicative factor to Q and a simple additive factor to entropy and free energies. This is usually neglected / omitted even though it is not 1.

$$Q = \frac{(q_{elec} q_{nucl} q_{trans})^N}{N!}$$

$$q_{trans} = \left(\frac{\sqrt{2\pi m kT}}{h^2} \right)^3 V = \left(\frac{2m kT \pi}{h^2} \right)^{3/2} V.$$

$$q_{elec} = w_{e1} + w_{e2} e^{-\beta \Delta \epsilon_{12}} + \dots$$

not important for chemical reactions. electronic partition function needs to be included because electronic states change upon chemical reaction

$$A = -kT \ln Q = -kT \ln \left(\frac{q^N}{N!} \right)$$

$$= -kT \ln \left(\frac{q^N}{N!} \right) = -NkT \ln \left(\frac{q}{N} \right)$$

$$= -NkT \left(\ln \left[\left(\frac{2m kT \pi}{h^2} \right)^{3/2} \frac{V}{N} \right] + \ln \left(w_{e1} + w_{e2} e^{-\beta \Delta \epsilon_{12}} \right) \right)$$

In Fermi electron system volume affects the electronic energy levels. Pressure comes from quantum mechanical attributes of these electrons.

$$\bar{E} = kT^2 \frac{d \ln Q}{dT} = NkT^2 \cdot \frac{3}{2} \frac{1}{T} + \frac{NkT^2 \cdot w_{e2} e^{-\Delta \epsilon_{12}/kT}}{q_{elec}} \frac{\Delta \epsilon_{12}}{kT^2}$$

$$\bar{E} = \frac{3}{2} NkT + \frac{Nw_{e2} e^{-\Delta \epsilon_{12}/kT} \Delta \epsilon_{12}}{q_{elec}}$$

contribution of to translational heat capacity $\left(\frac{\partial \bar{E}}{\partial T} \right)$ is $\frac{3}{2} Nk$

$$\bar{P} = kT \left(\frac{\partial \ln Q}{\partial V} \right) = kTN \cdot \frac{1}{V} + 0$$

since $q_{elec} q_{nucl}$ does not depend on container volume only on volume of atom.

$\bar{p}V = NkT$ ideal gas law relationship betⁿ p-V-T.

Note only contribution to pressure from translational degrees of freedom. Electronic and nuclear degrees of freedom do not contribute. \rightarrow much tighter wave-packets.

This is intuitive since pressure results from bombardment of walls by atoms of the gas.

Entropy $\frac{S}{k} = \ln Q + \frac{\bar{E}}{kT}$

$$\frac{S}{k} = \frac{3}{2} Nk + \frac{Nk \omega_{e2} \beta \Delta \epsilon_{12} e^{-\beta \Delta \epsilon_{12}}}{q_{elec}} + Nk \ln (\omega_{e1} + \omega_{e2} e^{-\beta \Delta \epsilon_{12}})$$

$$+ Nk \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V e}{N} \right]$$

$$S = \frac{3}{2} Nk + Nk \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V e}{N} \right] + S_{elec}$$

$$S = Nk \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + S_{elec}$$

Chemical potential $\mu = -\frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T} = -kT \frac{\partial \ln(q^N/N!)}{\partial N}$

$$= -kT \cdot \frac{\partial \ln(qe/N)^N}{\partial N} - kT \frac{\partial N \ln(qe/N)}{\partial N}$$

$$= -kT \left(\ln(qe/N) + N(-1) \frac{1}{N} \right)$$

$$= -kT \ln \frac{q}{N}$$

$$\mu = -kT \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V}{N} \right] - kT \ln q_{eq}$$

These for single particles unaffected by N. Since no interactions in ideal gas system

$$\mu = -kT \ln \left[\left(\frac{2\pi m kT}{h^2} \right)^{3/2} \frac{kT}{P} \right] - kT \ln q_{eqn}$$

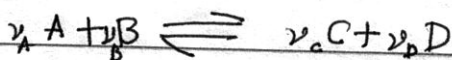
$$\mu = -kT \ln \left[\left(\frac{2\pi m kT}{h^2} \right)^{3/2} kT \right] - kT \ln q_{eqn} + kT \ln p$$

$$\therefore \mu = \mu_0 + kT \ln p \quad \mu = f(T, P)$$

μ_0 is chemical potential at a pressure of 1 atm (standard condition) for an ideal gas.

or for sol^{ns} $\mu = \mu_0 + kT \ln(c/c_0)$ where $c = \frac{N}{V} \Rightarrow$ concentration of molecules.

Using partition functions to evaluate equilibrium constants
Consider $r \rightleftharpoons$



we have determined in the past that equilibrium is described by

$$\sum_{\text{reactants}} \nu_i \mu_i = \sum_{\text{products}} \nu_j \mu_j$$

i.e. $\nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B = 0$

The partition function for the equilibrium mixture is given as:

$$Q(N_A, N_B, N_C, N_D, V, T) = \frac{(q_A)^{N_A}}{N_A!} \frac{(q_B)^{N_B}}{N_B!} \frac{(q_C)^{N_C}}{N_C!} \frac{(q_D)^{N_D}}{N_D!}$$

no. of molecules of each species at equilibrium.

$$\mu_x = -kT \left(\frac{\partial \ln Q}{\partial N_x} \right)_{N_y, V, T}$$

$$\therefore \mu_A = -kT \frac{\partial \ln (q_A e / N_A)^{N_A}}{\partial N_A}$$

$N_B, N_C, N_D =$ constant when chemical potential evaluated

$$\mu_A = -kT \ln \frac{q_A}{N_A}$$

\therefore equilibrium is given as.

In this case μ_0 is chemical potential for standard solⁿ of conc c_0

As concentration increases the chemical potential increases.

$$-kT \left[\ln \left[\frac{(q_C)^{\nu_C} (q_D)^{\nu_D}}{(N_C)^{\nu_C} (N_D)^{\nu_D}} \right] - \ln \left[\frac{(q_A)^{\nu_A} (q_B)^{\nu_B}}{(N_A)^{\nu_A} (N_B)^{\nu_B}} \right] \right] = 0$$

$$\therefore \frac{(N_C)^{\nu_C} (N_D)^{\nu_D}}{(N_A)^{\nu_A} (N_B)^{\nu_B}} = \frac{(q_C)^{\nu_C} (q_D)^{\nu_D}}{(q_A)^{\nu_A} (q_B)^{\nu_B}}$$

$$\therefore \frac{(N_C/V)^{\nu_C} (N_D/V)^{\nu_D}}{(N_A/V)^{\nu_A} (N_B/V)^{\nu_B}} = \frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}}$$

experimentally measurable.

known as an equilibrium constant K_c

calculate molecular partition function which has form $f(T)V$.

N/V represents a concentration.

ν represent stoichiometric coefficients

Sometimes for gaseous reactions, equilibrium constants are expressed in terms of pressures.

$$K_p(T) = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} = kT^{\nu_C + \nu_D - \nu_A - \nu_B} \frac{(N_C/V)^{\nu_C} (N_D/V)^{\nu_D}}{(N_A/V)^{\nu_A} (N_B/V)^{\nu_B}}$$

$$K_p(T) = kT^{\nu_C + \nu_D - \nu_A - \nu_B} K_c(T)$$

simply the difference in reactant & product moles.

"law" of equipartition of energy:

The energy of a molecule for a given degree of freedom is given as a quadratic function, e.g. of velocity ($\frac{1}{2}mv^2$) or of displacement ($\frac{1}{2}kx^2$)

\rightarrow potential energy
 \downarrow

kinetic energy

So the average energy per molecule for each degree of freedom:

$$\bar{\epsilon} = \frac{\int_{-\infty}^{\infty} \epsilon_x e^{-\beta \epsilon_x} dx}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_x} dx} \quad \text{where } \epsilon_x = ax^2$$

$\rightarrow x$ can be velocity or displacement.

$$= \frac{\int_{-\infty}^{\infty} ax^2 e^{-\beta ax^2} dx}{\int_{-\infty}^{\infty} e^{-\beta ax^2} dx}$$

$$= kT \frac{\int_{-\infty}^{\infty} \beta ax^2 e^{-\beta ax^2} dx}{\int_{-\infty}^{\infty} e^{-\beta ax^2} dx}$$

Substitute $y^2 = \beta ax^2$

$$\bar{\epsilon} = kT \frac{\int_{-\infty}^{\infty} y^2 e^{-y^2} dy / \sqrt{\beta a}}{\int_{-\infty}^{\infty} e^{-y^2} dy / \sqrt{\beta a}}$$

$$= kT \frac{\int_{-\infty}^{\infty} y^2 e^{-y^2} dy}{\int_{-\infty}^{\infty} e^{-y^2} dy} = kT \frac{\frac{1}{2} \sqrt{\pi} / 2}{\sqrt{\pi} / 2} = \frac{kT}{2}$$

$$\bar{\epsilon} = kT/2$$

So each degree of freedom (represented by a quadratic term in the Hamiltonian) contributes $kT/2$ per molecule to the total energy.

When no forces constrain motion \Rightarrow purely kinetic $\Rightarrow \frac{kT}{2}$ contribution

e.g. each translation degree of freedom contributes $\frac{kT}{2}$ per molecule
 vibration \rightarrow kinetic + potential energy $\Rightarrow kT$ per molecule.

The energies can be said to be almost continuously distributed.

$$\frac{E_{n+1} - E_n}{E_n} \ll 1$$

$$\therefore \frac{(n+1)^2 - n^2}{n^2} \ll 1 \quad \Rightarrow \quad \frac{2n+1}{n^2} \ll 1$$

$$\therefore \frac{2n}{n^2} \ll 1 \quad \therefore \frac{2}{n} \ll 1$$

Now $E_n = \frac{n^2 h^2}{8mL^2} \quad \therefore n = \frac{\sqrt{8mE}}{h} L$

At temperature T , average value of E_n is $\alpha(kT)$

$$\therefore \text{typical } n = \frac{\sqrt{8mkT}}{h} L$$

$$\therefore \frac{2}{n} \ll 1 \quad \text{implies} \quad \frac{2h}{\sqrt{8mkT}} L \ll 1$$

$$\therefore \frac{h}{\sqrt{2mkT}} \ll L$$

$$\therefore \left(\frac{h}{\sqrt{2mkT}} \right)^3 \ll L^3 \quad \text{LHS term is De-Broglie wavelength barring for a small factor of } 1/\sqrt{\pi}$$

$$\therefore \lambda^3 \ll V$$

λ thermal De-Broglie wavelength

When the particle (matter wave) "rarely sees" the boundaries of the container, the energies can be treated classically, as having a continuous distribution.