Chapter 20

Mixtures of Gases

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Partition Function of a Diatomic Gas

Energy of a molecule $E_{mol} = E_{trans} + E_{rot} + E_{vib}$

Particular energy level $\varepsilon_i = \varepsilon_{trans,i} + \varepsilon_{rot,i} + \varepsilon_{vib,i}$

Partition function of a **molecule** $Z_{mol} \equiv \sum_{i=1}^{n} g_i e^{\frac{-\varepsilon_i}{kT}} = \sum_{j=1}^{k} e^{\frac{-\varepsilon_j}{kT}}$

Partition Function of a Diatomic Gas

$$Z_{mol} = \sum_{j=1}^{k} e^{-(\varepsilon_{trans,j}+\varepsilon_{rot,j}+\varepsilon_{vib,j})/kT}$$

$$= \sum_{j=1}^{k} e^{-\varepsilon_{trans,j}/kT} \sum_{j=1}^{k} e^{-\varepsilon_{rot,j}/kT} \sum_{j=1}^{k} e^{-\varepsilon_{vib,j}/kT}$$

$$\therefore \boldsymbol{Z_{mol} = Z_{trans} Z_{rot} Z_{vib}}$$

The partition function of a molecule is the product of each term.

cf) Heat capacity

$$C_{V,mol} = C_{V,trans} + C_{V,rot} + C_{V,vib}$$

Partition Function of a System

System partition function $\mathbf{Z}_{sys}$ – Partition function of a system composed of N-particles

Partition function of a **molecule:**

$$Z_{mol} \equiv \sum_{i=1}^{n} g_i e^{\frac{-\varepsilon_i}{kT}} = Z_{trans} Z_{rot} Z_{vib}$$

Partition function of a **system:**
(for 1 ~ N particles)

$$Z_{sys} = Z_{mol}^{1} Z_{mol}^{2} \cdots Z_{mol}^{N} = \prod_{i=1}^{N} Z_{mol}^{i} = (Z_{mol})^{N}$$

If the system consists of indistinguishable particles, permutations of the particles should be considered. (next page)

Partition Function of a System

※ Distinguishable vs Indistinguishable particles

N – distinguishable particles: $Z_{sys} = Z^N$

N – indistinguishable particles (gas): $\boldsymbol{Z_{sys} = \frac{Z^N}{N!}}$

※ N! Permutations for indistinguishable particles

2 particles

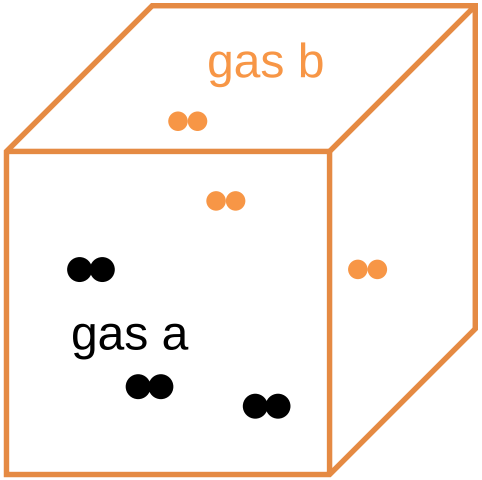
$$\underbrace{\begin{matrix} 1 & 2 \\ 2 & 1 \end{matrix}}_{2!\text{ ways}}$$

3 particles

$$\underbrace{\begin{matrix} 1 & 2 & 3 \\ 1 & 3 & 2 \\ 2 & 1 & 3 \\ 2 & 3 & 1 \\ 3 & 1 & 2 \\ 3 & 2 & 1 \end{matrix}}_{3!\text{ ways}}$$

Mixtures of Chemically Inert Perfect Gases

Assume an isolated vessel of volume V contains N_a molecules of gas ‘a’ and N_b molecules of gas ‘b’ $N = N_a + N_b$



※ A particular energy level of the system, ε_v

$$\varepsilon_v = \varepsilon_a + \varepsilon_b$$

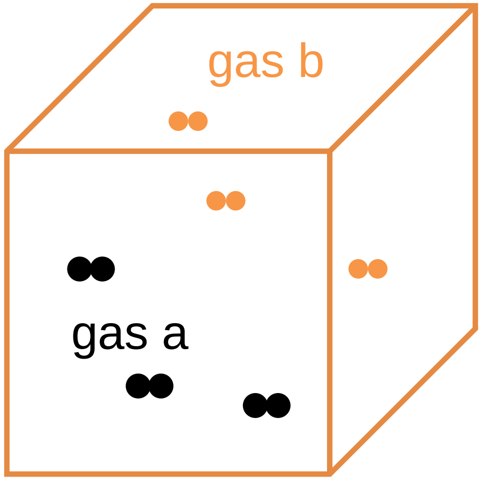
Where subscript a and b imply gas ‘a’ and ‘b’

The system partition function in vessel

$$Z_{sys} = \sum_{v=1}^{k} g_v e^{\frac{-\varepsilon_v}{kT}} = \boldsymbol{Z^a_{sys} Z^b_{sys}}$$

Where $\boldsymbol{Z^a_{sys}}$ means the system partition function of gas ‘a’

Mixtures of Chemically Inert Perfect Gases



The system partition function of each gas species

$$Z_{sys}^{a} = \frac{Z_a^{N_a}}{N_a!} \qquad Z_{sys}^{b} = \frac{Z_b^{N_b}}{N_b!}$$

$$Z_{sys} = Z_{sys}^{a} Z_{sys}^{b} = \frac{Z_a^{N_a} Z_b^{N_b}}{(N_a + N_b)!} \quad or \quad \frac{Z_a^{N_a} Z_b^{N_b}}{N_a!\, N_b!}$$

Indistinguishable (treated as one kind) distinguishable

Entropy of the system

$$S_{sys} = \frac{U}{T} + k \ln Z_{sys}$$

$$S_{ind} = \frac{U}{T} + kN_a \ln Z_a + kN_b \ln Z_b - k \ln(N_a + N_b)!$$

for **indistinguishable** molecules $(a = b)$

$$S_d = \frac{U}{T} + kN_a \ln Z_a + kN_b \ln Z_b - k \ln(N_a!\, N_b!)$$

for **distinguishable** molecules $(a \neq b)$

Mixtures of Chemically Inert Perfect Gases

Because numerically $N_a!\,N_b! < (N_a + N_b)!$, thus $\boldsymbol{S_d} > \boldsymbol{S_{ind}}$

$$\Delta S_{mix} = S_d - S_{ind} > 0$$

The higher entropy of a mixture of operationally distinguishable elements – the entropy of mixing – is seen to be a direct consequence of their **distinguishability**.

Mixtures of Chemically Inert Perfect Gases

Use Stirling's approximation $\ln N! = N \ln N - N$

$$\Delta S_{mix} = S_d - S_{ind}$$

$$= k(N_a + N_b)\ln(N_a + N_b) - kN_a \ln N_a - kN_b \ln N_b$$

Note that molecules $N_a = n_a \mathbf{N_A}$ where $\mathbf{N_A}$ is the Avogadro # (6.022 X 10^{23}/mol)

$$\Delta S_{mix} = k(n_a + n_b)\mathbf{N_A} \ln(n_a + n_b) - kn_a\mathbf{N_A} \ln n_a - kn_b\mathbf{N_A} \ln n_b$$

Mixtures of Chemically Inert Perfect Gases

$$\Delta S_{mix} = k(n_a + n_b)\mathbf{N_A}\ln(n_a + n_b) - kn_a\mathbf{N_A}\ln n_a - kn_b\mathbf{N_A}\ln n_b$$

$$= (n_a + n_b)R\ln(n_a + n_b) - n_aR\ln n_a - n_bR\ln n_b \qquad (\because k\mathbf{N_A} = R)$$

$$= -n_aR\ln\frac{n_a}{(n_a + n_b)} - n_bR\ln\frac{n_b}{(n_a + n_b)}$$

Since $(n_a + n_b)R = PV/T$

Mole fraction $x_a = n_a/(n_a + n_b)$ and $x_b = n_b/(n_a + n_b)$

Entropy change of mixing in perspective of statistical thermodynamics

$$\therefore \boldsymbol{\Delta S_{mix} = -\frac{PV}{T}(x_a \ln x_a + x_b\, ln\, x_b) > 0} \qquad x_a < 1, x_b < 1$$