Thermodynamic functions for Monoatomic gases

The canonical ensemble partition function of monoatomic gases can be written in terms of the individual atomic partition functions as:-

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

where $q(V,T)$ for monoatomic gases is $q_{trans}\, q_{elec}\, q_{nucl}$

Helmholtz Free Energy, $A(N,V,T)$

$$A(N,V,T) = -kT\ln(Q(N,V,T))$$

$$= -KT\{N\ln(q_{trans}\, q_{elec}\, q_{nucl}) - (N\ln(N) - N)\}$$

$$= -NKT\{\ln(q_{trans}\, q_{elec}\, q_{nucl}) - \ln(\tfrac{N}{e})\}$$

$$\Rightarrow A(N,V,T) = -NKT\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{Ve}{N}\right)\right] - NKT\ln(w_{e_1} + w_{e_2}e^{-\beta\Delta E_{12}})$$

$$-NKT\ln(w_{n_1}) + \ldots$$

Internal energy of monoatomic gases

$$\bar{E} = KT^2\left(\frac{\partial \ln Q(N,V,T)}{\partial T}\right)_{N,V}$$

$$\Rightarrow \ln(Q(N,V,T)) = N\ln(q_{trans}\, q_{elec}\, q_{nucl}) - (N\ln(N) - N)$$

$$\Rightarrow \ln(Q(N,V,T)) = N\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{Ve}{N}\right)\right] - N\ln(w_{e_1} + w_{e_2}e^{-\beta\Delta E_{12}} \ldots)$$

$$-NKT\ln(w_{n_1}) + \ldots$$

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$$\Rightarrow \bar{E} = NKT^2 \times \left(\frac{3}{2T}\right) - NKT^2\left(\frac{\omega e_2 e^{-\beta\Delta E_{12}}}{q_{elec}}\right) \times \left(\frac{-1}{KT^2}\right)$$

$$\bar{E} = \frac{3NKT}{2} + \frac{N\omega e_2 e^{-\beta\Delta E_{12}}}{q_{elec}} + \ldots$$

Ignoring nuclear partition function because $q_{nuc} = \omega n_1$ at STP.

Pressure of monoatomic gases

$$\bar{p} = KT\left(\frac{\partial \ln(Q(N,V,T))}{\partial V}\right)_{N,T}$$

$$\Rightarrow \bar{p} = NKT \times \left(\frac{1}{V}\right) = \frac{NKT}{V}$$

Entropy of monoatomic gases

$$S = K\ln(Q(N,V,T)) + KT\left(\frac{\partial \ln Q(N,V,T)}{\partial T}\right)_{N,V}$$

$$TS = E - A$$

$$\Rightarrow S = \frac{E}{T} - \frac{A}{T}$$ (where E is internal energy and A is Helmholtz Free energy)

$$\Rightarrow S = \frac{3}{2}NK + \left(\frac{NK\omega e_2\, \beta\Delta E_{12}\, e^{-\beta\Delta E_{12}}}{q_{elec}}\right) + NK\left(\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{Ve}{N}\right)\right]\right.$$

$$+ NK\ln\left(\omega e_1 + \omega e_2 e^{-\beta\Delta E_{12}}\right)$$

Sackur-Tetrode Equation

$$S = NK\left(\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{Ve}{N}\right)\right] + \frac{3}{2}\right) + NK\left(\ln\left(w_{e_1} + w_{e_2}e^{-\beta\Delta E_{12}}\right)\right)$$
$$+ NK\left(\frac{w_{e_2}\beta\Delta E_{12}e^{-\beta\Delta E_{12}}}{q_{elec}}\right)$$

$$\Rightarrow S = NK\left(\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{Ve^{5/2}}{N}\right)\right]\right) + S_{elec}$$

Chemical potential of monoatomic gases

$$\mu = -KT\left(\frac{\partial \ln Q(N,V,T)}{\partial N}\right)_{V,T}$$

$$\Rightarrow \ln Q(N,V,T) = N\ln\left(q_{trans}\,q_{elec}\,q_{nucl}\right) - \left(N\ln(N) - N\right)$$
$$= N\left(\ln\left(q_{trans}\,q_{elec}\,q_{nucl}\right) + \ln\left(\frac{e}{N}\right)\right)$$

$$\Rightarrow \left(\frac{\partial \ln(Q(N,V,T))}{\partial N}\right)_{V,T} = \ln\left(q_{trans}\,q_{elec}\,q_{nucl}\right) - \left(\left(N\cdot\frac{1}{N}\right) + \ln(N) - 1\right)$$
$$= \ln\left(\left(q_{trans}\,q_{elec}\,q_{nucl}\right)/N\right)$$

$$\Rightarrow \mu = -KT\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left(\frac{V}{N}\right)\right] - KT\ln\left(q_{elec}\,q_{nucl}\right)$$

$$\Rightarrow \mu = \underbrace{-KT\left(\ln\left[\left(\frac{2\pi mKT}{h^2}\right)^{3/2}KT\right] - \ln\left(q_{elec}\,q_{nucl}\right)\right)}_{\mu_0(T)} + KT\ln p$$

[Since $V = \frac{NKT}{p}$ for ideal gases]

or $\boxed{\mu = \mu_0(T) + KT\ln p}$ → classical Thermodynamics Equation