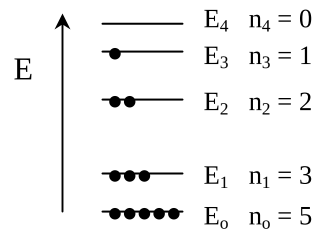
<u>Entropy and the Partition Function</u>

$$S = \frac{k}{\mathcal{N}} \ln \mathcal{W}_{max} \qquad \text{(Canonical ensemble)}$$

$$\mathcal{W} = \frac{\mathcal{N}!}{n_o! n_1! n_2! \ldots}$$

$$\ln \mathcal{W} = \ln \mathcal{N}! - \sum_{i=0}^{\infty} \ln n_i! \qquad \text{(sum over all energy states)}$$



Sterling's Formula: $\ln x! = x \ln x - x$ $\qquad \ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \Sigma\,(n_i \ln n_i - n_i)$

$\Sigma\, n_i = \mathcal{N}$ giving $\qquad \ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \Sigma\, n_i \ln n_i$

$$n_i = \frac{\mathcal{N}}{Q} e^{-E_i/kT} \qquad \ln n_i = \ln \mathcal{N} - \ln Q - E_i/kT$$

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \Sigma\, n_i \ln \mathcal{N} + \Sigma\, n_i \ln Q + \Sigma \frac{n_i E_i}{kT}$$

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} \ln \mathcal{N} + \mathcal{N} \ln Q + \frac{\mathcal{E}}{kT}$$

$$S = \frac{k}{\mathcal{N}} \ln \mathcal{W}_{max} = k \ln Q + \frac{\mathcal{E}}{\mathcal{N}T} = k \ln Q + \frac{U - U(0)}{T} \qquad U(0) \text{ at } 0\text{ K}$$

<u>ideal gas</u>: $U - U(0) = {}^3/_2\, nRT = {}^3/_2\, NkT \qquad S = k \ln Q + {}^3/_2\, nR$

$$Q = \frac{q^N}{N!} \qquad N! \cong (N/e)^N \qquad Q \cong \left(\frac{qe}{N}\right)^N \qquad \text{ideal monatomic: } q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$S = Nk \ln\left(\frac{qe}{N}\right) + {}^3/_2\, nR = nR \ln\left[\frac{(2\pi mkT)^{3/2} e}{Nh^3} V\right] + {}^3/_2\, nR \qquad m \sim \text{kg molecule}^{-1},\ V \sim m^3$$

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per mole: $N = N_A$ $\quad n = 1$ mol $\quad N_A k = R$ $\quad {}^3/_2 = \ln e^{3/2}$

$$S_m = R \ln\left[\frac{(2\pi mkT)^{3/2} e^{5/2}}{N_A h^3} V_m\right] \qquad \text{Sackur-Tetrode Equation}$$

$$S_m = R \ln V_m + {}^3/_2\, R \ln T + {}^3/_2\, R \ln \mathcal{M} + R \ln\left[\frac{(2\pi k(1\text{ kg}/1000\text{ g})/N_A)^{3/2} e^{5/2} (1\text{ m}^3/1000\text{ L})}{N_A h^3}\right]$$

$$S_m = R \ln(V_{m/L}) + {}^3/_2\, R \ln T + {}^3/_2\, R \ln(\mathcal{M}_{/g\ mol^{-1}}) + 11.1037\text{ J K}^{-1}\text{ mol}^{-1}$$

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cst. T: $\Delta S_m = R \ln(V_2/V_1)$ $\qquad$ cst. V: $\Delta S_m = {}^3/_2\, R \ln(T_2/T_1) = C_v \ln(T_2/T_1)$

$P° = 1$ bar $\quad V^\circ_m = RT/P° = 0.0247890\text{ m}^3 = 24.7890$ L at 298.15 K

$S^\circ_{m,298.15\,K} = 26.6929 + 71.0587 + {}^3/_2\, R \ln(\mathcal{M}_{/g\ mol^{-1}}) + 11.1037\text{ J K}^{-1}\text{ mol}^{-1}$ (translation)