## **Entropy and the Partition Function**

$$S = \frac{k}{\mathcal{N}} ln \ \mathcal{W}_{max}$$

(Canonical ensemble)

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

$$\label{eq:lnw} \begin{array}{l} ln \ \mathcal{W} = ln \ \mathcal{M}! - \sum\limits_{i=0}^{\infty} ln \ n_i! \qquad \text{(sum over all energy states)} \end{array}$$

$$E_1 \quad n_1 = 3$$

$$E_0 \quad n_0 = 5$$

Sterling's Formula:  $\ln x! = x \ln x - x$ 

$$ln \mathcal{W} = \mathcal{N}ln \mathcal{N} - \mathcal{N} - \sum (n_i ln n_i - n_i)$$

$$\sum n_i = \mathcal{N}$$
 giving

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_{i} n_{i} \ln n_{i}$$

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

$$ln \; n_i = ln \; \mathcal{N} - ln \; Q - E_i /_{kT}$$

$$ln \mathcal{W} = \mathcal{N}ln \mathcal{N} - \sum_{i} n_{i} ln \mathcal{N} + \sum_{i} n_{i} ln Q + \sum_{i} \frac{n_{i} E_{i}}{kT}$$

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

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

U(0) at 0 K

ideal gas: 
$$U - U(0) = \frac{3}{2} nRT = \frac{3}{2} NkT$$
  $S = k ln Q + \frac{3}{2} nR$ 

$$S = k \ln Q + \frac{3}{2} nR$$

$$Q = \frac{q^N}{N!}$$

$$N! \cong (N/e)^N$$

$$Q \cong \left(\frac{qe}{N}\right)^N$$

$$\overline{Q = \frac{q^N}{N!}} \hspace{1cm} N! \; \cong \left( \frac{N}{e} \right)^N \hspace{1cm} Q \cong \left( \frac{qe}{N} \right)^N \hspace{1cm} \text{ideal monatomic:} \; q_t = \frac{\left( 2\pi mkT \right)^{3/2}}{h^3} \, V$$

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

$$m \sim kg \text{ molecule}^{-1}, V \sim m^3$$

per mole:  $N = N_A$ 

$$n = 1 \text{ mol}$$

$$N_A k = R$$

$$^{3}/_{2} = \ln e^{3/2}$$

$$S_{m} = R ln \left[ \frac{(2\pi mkT)^{3/2}e^{5/2}}{N_{A}h^{3}} V_{m} \right]$$

$$S_{m} = R \, ln \, V_{m} + {}^{3}\!/_{2} \, R \, ln \, T + {}^{3}\!/_{2} \, R \, ln \, \mathcal{M} + R \, ln \Bigg[ \frac{(2\pi k (1 \, kg/1000 \, g)/N_{A})^{3/2} e^{5/2} (1 \, m^{3}/1000 \, L)}{N_{A} h^{3}} \Bigg]$$

$$S_m = R \ln(V_{m/L}) + \frac{3}{2} R \ln T + \frac{3}{2} R \ln(\mathcal{M}_{g \text{ mol}^{-1}}) + 11.1037 \text{ J K}^{-1} \text{ mol}^{-1}$$

cst. T: 
$$\Delta S_m = R \ln(V_2/V_1)$$

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$$\Delta S_m = R \ln(V_2/V_1)$$
 cst. V:  $\Delta S_m = \frac{3}{2} R \ln(T_2/T_1) = C_v \ln(T_2/T_1)$ 

$$\begin{array}{lll} \hline P^{\circ} = 1 \ bar & V_{m}^{\circ} = RT/P^{\circ} = 0.0247890 \ m^{3} = 24.7890 \ L \ \ at \ 298.15 \ K \\ S_{m,298.15 \ K}^{\circ} = 26.6929 + 71.0587 + {}^{3}\!/_{2} \ R \ ln(\mathcal{M}_{/g \ mol^{-1}}) + 11.1037 \ J \ K^{-1} \ mol^{-1} \end{array}$$

$$S_{m,298.15 \text{ K}}^{\circ} = 26.6929 + 71.0587 + \frac{3}{2} \text{R} \ln(\mathcal{M}_{\text{g mol}^{-1}}) + 11.1037 \text{ J K}^{-1} \text{ mol}^{-1}$$

(translation)