

GIBBS ENERGY

$$G = -k_B T \left[\ln Q - V \left(\frac{\partial \ln Q}{\partial V} \right)_V \right]$$

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

$$\ln Q = N \ln q - \ln N!$$

$$\ln N! = N \ln N - N$$

$$N! = e^{-N} N^N = \left(\frac{N}{e} \right)^N$$

$$Q = \left(\frac{q e}{N} \right)^N$$

$$G = -k_B T \left[\ln Q - V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right]$$

$$\ln Q = N \ln \left(\frac{q}{N} \right)$$

$$\ln Q = N \ln q + N \ln \left(\frac{e}{N} \right)$$

$$\left(\frac{\partial \ln Q}{\partial V} \right)_T = N \left(\frac{\partial \ln q}{\partial V} \right) = \frac{N}{q} \left(\frac{\partial q}{\partial V} \right)_T$$

$$G = -k_B T \left[N \ln q + N \ln \left(\frac{e}{N} \right) - V \frac{N}{q} \left(\frac{\partial q}{\partial V} \right)_T \right]$$

$$= -k_B T N \ln \left(\frac{q}{N} \right)$$

$$= -k_B T \left[\ln q - \frac{V}{q} \left(\frac{\partial q}{\partial V} \right)_T \right] N$$

$$= -k_B T N \ln \left(\frac{q}{N} \right)$$

$$= -k_B T N \left(\frac{\partial}{\partial V} V \ln q \right)$$

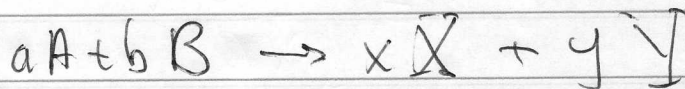
$$q_T \sim V$$

$$V \left(\frac{\partial q_T}{\partial V} \right)_T = q_T$$

$$G = -k_B T N \left[1 - \ln N + \ln q - 1 \right]$$

$$G = -N k_B T \ln \left(\frac{q}{N} \right)$$

$$\Delta G^\circ = -RT \ln K \quad (N = N_A)$$



$$\Delta G^\circ = -RT \ln \left[\frac{\left(\frac{q_X^\circ}{N}\right)^x \left(\frac{q_Y^\circ}{N}\right)^y}{\left(\frac{q_A^\circ}{N}\right)^a \left(\frac{q_B^\circ}{N}\right)^b} \right]$$

SHIFT THE ZERO ENERGY

So FOR q_{TVE}

$$q_{TVE} = \Omega^{\beta \epsilon_i} \left[1 + \Omega^{-\beta \bar{\epsilon}} + \Omega^{-2\beta \bar{\epsilon}} + \dots \right]$$

$$\Delta G^\circ = -RT \ln \left[\frac{\left(\frac{q_X^\circ}{N}\right)^x \left(\frac{q_Y^\circ}{N}\right)^y}{\left(\frac{q_A^\circ}{N}\right)^a \left(\frac{q_B^\circ}{N}\right)^b} \Omega^{-\beta \Delta \epsilon} \right]$$

FOR OXYGEN f_{O_2} IS
RELEVANT

$$f_{\text{O}_2} = \frac{1}{Q} e^{-\beta \epsilon_{\text{O}_2}} \left[g_{\text{O}_2}^0 + \sum_{i=1}^{\infty} g_{\text{O}_2}^i e^{-\beta(\epsilon_i^{\text{O}_2} - \epsilon_{\text{O}_2}^0)} \right]$$

FOR

0 $\epsilon_i - \epsilon_0 / \text{eV}$ kT

0.02 232K

0.03 348K

1.97 22859K

HELMHOLTZ ENERGY

$$A = -k_B T \ln Q$$

$$A = -k_B T \ln \left\{ \left(\frac{q_T q_R q_V q_C}{N} \right)^N \right\}$$

$$= -N k_B T \ln \left\{ \frac{V q_R q_V q_C}{N \Lambda(T)^3} \right\}$$

A IS AN EXTENSIVE VARIABLE

$$\Rightarrow \begin{array}{l} N \rightarrow 2N \\ V \rightarrow 2V \end{array} \left\{ \Rightarrow A \rightarrow 2A \right.$$

WITHOUT THE $N!$, A IS NOT AN
EXTENSIVE VARIABLE!

$$A = -k_B T \ln Q$$

$$= -k_B T \ln \left(\frac{q}{N} \right)^N$$

$$= -N k_B T \ln q$$

$$- k_B T N \ln \left(\frac{e}{N} \right)$$

$$= -N k_B T \ln q - \underbrace{k_B T N \ln \left(\frac{e}{N} \right)}_?$$