GIBBS ENERGY

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

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

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

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

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

$$\boxed{Q = \left(\frac{qe}{Ne}\right)^N}$$

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

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

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

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

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

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

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

$$q_T \sim V$$

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

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

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

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

$$aA + bB \rightarrow xX + yY$$

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

SHIFT THE ZERO ENERGY

SO FOR q_v

$$q_{vi} = e^{\beta \varepsilon_i} \left[1 + e^{-\beta \bar{\nu}} + e^{-2\beta \bar{\nu}} + \cdots \right]$$

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

FOR OXYGEN q_{elec} IS RELEVANT

$$q_e = e^{-\beta \varepsilon_0^e}\left[g_e^0 + \sum_{i=1}^{n} g_i^e e^{-\beta(\varepsilon_i^e - \varepsilon_0^e)}\right]$$

FOR

O	$\varepsilon_1 - \varepsilon_0$ / eV	$k_B T$
	0.02	232K
	0.03	348K
	1.97	22859K

HELMHOLTZ ENERGY

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

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

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

A IS AN EXTENSIVE VARIABLE

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

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

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

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

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

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

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