

Chapter 11 The Diffusive Interaction

Recall

$$\delta E = T \delta S - p \delta V + \mu \delta N$$

These are more familiar to you.

↖ focus of this chapter

↖ Not so familiar so need to make sure we have the concept.

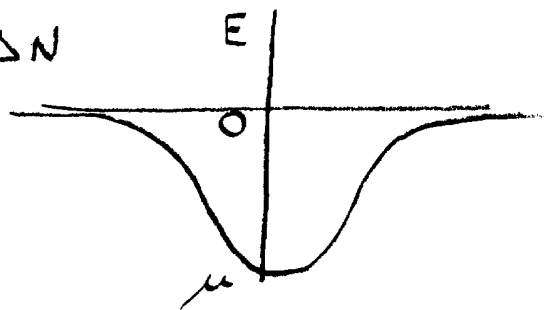
A. Chemical Potential

- Consider water molecules from space (energyless) being added to a glass of water.
- It falls into a potential well due to electrostatic forces
- It gains kinetic energy which ends up as thermal motion.
- Energy is conserved:

$$\Delta E = 0 = \Delta Q - \overset{\uparrow}{dW}_0 + \mu \Delta N$$

$$\therefore \Delta Q = -\mu \Delta N$$

↖ $\mu < 0$



Example

Add 10^{21} molecules of acid to 1 l of H_2O .

$\Delta T = +0.1^\circ C$ as a result.

What is μ ? Neglect self-interaction of acid.

$$\mu = -\frac{\Delta Q}{\Delta N} = -\frac{mC\Delta T}{\Delta N} = -\frac{1000 \text{ gm} \times \frac{1 \text{ cal}}{\text{gm}^\circ C} \times 0.1^\circ C}{10^{21}}$$

$$= -\frac{10^2 \text{ cal}}{10^{21}} = -2.6 \text{ eV}$$

B. Influence of $T, P + N$

μ should vary as $f_n(T, P, N)$

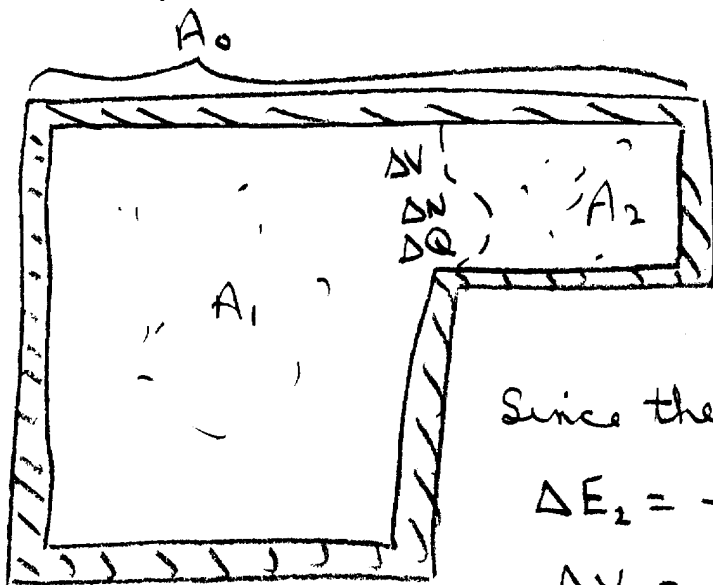
- $T \uparrow \Rightarrow$ more motion \Rightarrow more chemical interaction

- $P \uparrow \Rightarrow$ closer packing \Rightarrow more interaction

- $N \uparrow \Rightarrow$ higher concentration \Rightarrow " "

The amount + sign are case dependent.

C. Equilibrium Conditions



$$\Delta E = T \Delta S - P \Delta V + \mu \Delta N$$

$$\Delta S = \frac{1}{T} \Delta E + \frac{P}{T} \Delta V - \frac{\mu}{T} \Delta N$$

Since the system is isolated,

$$\Delta E_2 = -\Delta E_1$$

$$\Delta V_2 = -\Delta V_1$$

$$\Delta N_2 = -\Delta N_1$$

↑ Interacting system

$$\therefore \Delta S_0 = \Delta S_1 + \Delta S_2 = \frac{1}{T_1} \Delta E_1 + \frac{1}{T_2} \Delta E_2 + \dots$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta E_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \Delta N_1$$

At equilibrium, $\Delta S_0 = 0$

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\therefore since E, V & N are independent variables,

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \Rightarrow \quad T_1 = T_2$$

$$\frac{P_1}{T_1} - \frac{P_2}{T_2} = 0 \quad \Rightarrow \quad P_1 = P_2$$

$$\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} = 0 \quad \Rightarrow \quad \mu_1 = \mu_2$$

D. Approach to Equilibrium

Further, in the approach to equilibrium, $\Delta S_0 > 0$.

And we have $\Delta E_1 = \Delta Q_1 - P_1 \Delta V_1 + \mu_1 \Delta N_1$,

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$$\begin{aligned} \Delta S_0 &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) (\Delta Q_1 - P_1 \Delta V_1 + \mu_1 \Delta N_1) \\ &\quad + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \Delta N_1 > 0 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta Q_1 + \frac{1}{T_2} (P_1 - P_2) \Delta V_1 - \frac{1}{T_2} (\mu_1 - \mu_2) \Delta N_1 \end{aligned}$$

Again, since Q , V & N are independent variables,

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta Q_1 > 0 \Rightarrow \text{if } \Delta Q_1 < 0 \text{ then } T_1 > T_2$$

(heat flows from hot \rightarrow cold)

$$(P_1 - P_2) \Delta V_1 > 0 \Rightarrow \text{if } \Delta V_1 > 0 \text{ then } P_1 > P_2$$

(higher P expands)

$$-(\mu_1 - \mu_2) \Delta N_1 > 0 \Rightarrow \text{if } \Delta N_1 > 0 \text{ then } \mu_2 > \mu_1$$

(particles flow to lower potential)

Note: had to do the ΔE_1 substitution to put in terms of ΔQ_1 , some could focus on heat flow, not overall energy flow.

E. Chemical Potential and the Number of Accessible States

$$\text{from } dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$-\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right)_{E,V} \Rightarrow -\mu = T \left. \frac{\partial S}{\partial N} \right)_{E,V}$$

$$\therefore -\mu = kT \left. \frac{\partial \ln \Omega}{\partial N} \right)_{E,V}$$

So if we add energyless particles to a system:

$$\Delta(\ln \Omega) = -\frac{\mu}{kT} \Delta N$$

$$\ln \Omega_2 - \ln \Omega_1$$

$$\ln \frac{\Omega_2}{\Omega_1} \Rightarrow \frac{\Omega_2}{\Omega_1} = e^{-\frac{\mu \Delta N}{kT}}$$

Example

$$\text{If } \mu = -3.0 \text{ eV} \text{ + } T = 300 \text{ K}$$

What is $\frac{\Omega_2}{\Omega_1}$ when 1 particle is added?

Soln:

$$\frac{\Omega_2}{\Omega_1} = e^{3 / (0.846 \times 10^{-4} \times 300)} = e^{116} = 2.4 \times 10^{50} !$$

ie huge increase in # states just by adding 1 particle !

F. Salty Water + Snowflakes

Example of salt in water:

$$\mu_{\text{NaCl in salt}} \approx -3.0 \text{ eV}$$

$$\mu_{\text{NaCl in water}} \approx -3.1 \text{ eV}$$

ie salt is attracted to salt but it is more attracted to water.

as more and more salt dissolves,

$\mu_{\text{solution}} \uparrow$ until there is no potential advantage to dissolve

The same thing happens to ice crystals in cold saturated air (snow flakes grow)