

THERMO

08/29/22

LAWS OF THERMODYNAMICS

First Law

$$dU = dQ - PdV$$

Work \rightarrow Negative when done by the system

Second Law

$$dS \geq \frac{dQ}{T} \rightarrow \text{Irreversible process}$$

$$dS = \frac{dQ}{T} \rightarrow \text{Reversible Process}$$

* La primera ley no impide que el calor pueda ir de menor temperatura a mayor temperatura, la segunda ley si.

for molecular

$$S = k_B \ln \sigma$$

$\sigma \rightarrow$ Number of ways of arranging the system

Phase rule

$$F + \pi = C + 2$$

Degree of freedom

number of phases

number of components

(e.g.) Water boiling $\rightarrow F + 2 = 1 + 2 \rightarrow F = 1$ degree

Water + ethanol mixture boiling

$$F + 2 = 2 + 2 \rightarrow F = 2$$

Triple Point

$$F + 3 = 1 + 2 \rightarrow F = 0$$

P - V - T behavior

Ideal gas

$$Pv = RT$$

molar volumen

$$PV = nRT$$

Total volumen

Equations of state

Polynomial EOS (van der Waals)
Virial EOS
Corresponding States

Virial EOS:

$$Z = P_v / RT$$

for ideal gas

$$Z = 1$$

for real gas

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

Pressure expansion

$$Z = 1 + B'P + C'P^2 + \dots$$

Corresponding States

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c} \rightarrow Z = Z(P_r, T_r)$$

* All materials at same reduced pressure and reduce temperature have the same Z

$$Z = Z^0 + \omega Z^1, \quad \omega = -1.0 - \log(P_r^{sat}) \Big|_{T_r=0.7}$$

Temperature Scale: Absolute Zero

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow \Delta U = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1}^{T_2} C_v dT$$

$$dH = \int C_p dT \quad \Delta H = \int_{T_1}^{T_2} C_p(T) dT$$

CLASSICAL THERMODYNAMICS

Consider a reversible process in a closed system

$$dU = dQ - PdV \quad (\text{First Law})$$

$$dQ = Tds \quad (\text{Second Law})$$

$$dU = Tds - PdV$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = Tds - PdV + PdV + VdP$$

$$dH = Tds + VdP$$

$$A = U - TS$$

$$dA = dU - Tds - SdT$$

$$dA = Tds - PdV - Tds - SdT$$

$$dA = -SdT - PdV$$

$$G = H - TS$$

$$dG = dH - Tds - SdT$$

$$dG = Tds + VdP - Tds - SdT$$

$dG = VdP - SdT \rightarrow$ La favorita porque puedes controlar Presión y Temperatura muy facil (en un proceso)

Maxwell's Relations CATCTUS

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$df = Mdx + Ndy$$

$$\frac{\partial M}{\partial y} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial N}{\partial x}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \rightarrow \text{Relación de Maxwell aplicada a } dU$$

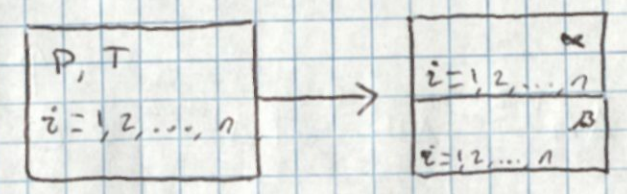
You can measure the partials in the dotted boxes

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial T}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

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PHASE EQUILLIBRIUM



Second Law

$$dS \geq \frac{dQ}{T}$$

$$Tds \geq dQ$$

$$Tds \geq dU + PdV$$

At constant S and V

$$dU \leq 0$$

$$-dU + Tds - PdV \geq 0$$

$$dU - Tds + PdV \leq 0$$

* Constant S is not easy in practice, so we change a little

$$H = U + PV$$

At constant S and P

$$dH = dU + PdV + VdP$$

$$dH \leq 0$$

$$-dU - PdV = VdP - dH$$

* Again, constant S is hard to set in practical ways

$$-Tds \leq VdP - dH$$

$$dH - Tds - VdP \leq 0$$

$= U - TS$
 $= dU - Tds - SdT$

At constant T and V
 $dA \leq 0$

$-dA - SdT - PdV \geq 0$ | * Better than the previous two

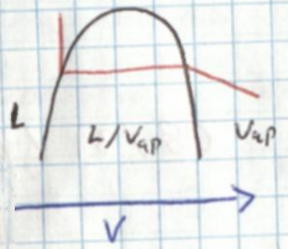
can go better with G

$= H - TS$
 $= dH - Tds - SdT$

At constant T and P
 $dG \leq 0$

$= U + PV - TS$
 $= dU + PdV + VdP - Tds - SdT$
 $+ SdT - VdP \leq 0$

Two phase diagram isotherm



At coexistence
 $G = \text{constant}$
 $G^L = G^V$
 $dG^L = dG^V$

$T, P = P^{sat}$
 Constant G

$dP^{sat} - S^L dT = V^V dP^{sat} - S^V dT$
 $\frac{dP^{sat}}{dT} = \frac{S^V - S^L}{V^V - V^L} = \frac{\Delta S^{V-L}}{\Delta V^{V-L}}$
 Using $\Delta G^{V-L} = \Delta H^{V-L} - T\Delta S^{V-L} = 0$

$\frac{dP^{sat}}{dT} = \frac{\Delta H^{V-L}}{T\Delta V^{V-L}}$ } Clapeyron Eqn
 Using $\Delta V^{V-L} = V^V - V^L \approx V^V$

Volume of vapour is bigger than volume of liquid

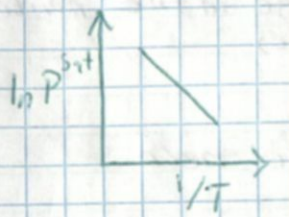
Assumption: Low pressure (ideal gas)
 $V^L \approx V^V = \frac{RT}{P^{sat}}$

If we substitute on Clapeyron:

$\Delta H^{V-L} = \frac{T^2 R}{P^{sat}} \frac{dP^{sat}}{dT} = R \frac{d \ln P^{sat}}{d(\frac{1}{T})}$
 We use $d(\frac{1}{T}) = -\frac{1}{T^2} dT$

$= -R \frac{d \ln P^{sat}}{d(\frac{1}{T})}$ } Clausius-Clapeyron

If we plot $\ln P^{sat}$ vs $1/T$



This suggests:

$\ln P^{sat} = A - \frac{B}{T} \rightarrow \ln P^{sat} = A - \frac{B}{T+C}$
 Antoine

$G \rightarrow$ Capital is for total system

$g \rightarrow$ Lower is for molar (single component)

SINGLE PHASE, CLOSED SYSTEM

per mol: $dg = v dP - s dT$

$n_t g = G$

Total: $dG = V dP - S dT$

$d(n_t g) = (n_t v) dP - (n_t s) dT$

$\frac{\partial (n_t g)}{\partial P} \Big|_T = n_t v$; $\frac{\partial (n_t g)}{\partial T} \Big|_P = -n_t s$

OPEN SYSTEM, SINGLE PHASE, MULTICOMPONENT

$n_t = n_1 + n_2 + \dots + n_m = \sum_{i=1}^m n_i$

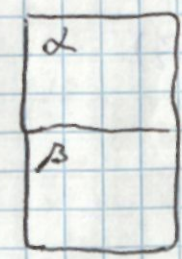
$n_t g = f(T, P, n_1, n_2, \dots, n_m)$

$d(n_t g) = \frac{\partial (n_t g)}{\partial T} \Big|_{P, n_i} dT + \frac{\partial (n_t g)}{\partial P} \Big|_{T, n_i} dP + \frac{\partial (n_t g)}{\partial n_1} \Big|_{P, T, n_{j \neq 1}} dn_1 + \frac{\partial (n_t g)}{\partial n_2} \Big|_{P, T, n_{j \neq 2}} dn_2 + \dots$

$\mu_i = \frac{\partial (n_t g)}{\partial n_i} \Big|_{P, T, n_{j \neq i}}$ \rightarrow Chemical Potential of i

Constant T, P

For each phase



$T^\alpha = T^\beta$
 $\mu_i^\alpha = \mu_i^\beta$
 $P^\alpha = P^\beta$

$d(n_t g)^\alpha = (n_t v)^\alpha dP - (n_t s)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$
 $d(n_t g)^\beta = (n_t v)^\beta dP - (n_t s)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$

We add both

$d(n_t g)^\alpha + d(n_t g)^\beta = d(n_t g) = (n_t v) dP - (n_t s) dT + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$
 Entire system

$$A = U - TS$$

At constant T and V

$$dA = dU - TdS - SdT$$

$$dA \leq 0$$

~~It can go better with G~~ * Better than the previous two

It can go better with \bar{G}

$$\bar{G} = H - TS$$

At constant T and P

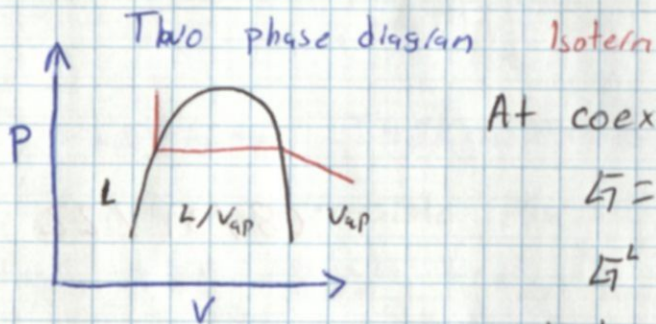
$$d\bar{G} = dH - TdS - SdT$$

$$d\bar{G} \leq 0$$

$$\bar{G} = U + PV - TS$$

$$d\bar{G} = dU + PdV + VdP - TdS - SdT$$

$$d\bar{G} + SdT - VdP \leq 0$$



At coexistence

$$\bar{G} = \text{constant}$$

$$\bar{G}^L = \bar{G}^V$$

$$T, P = P^{sat}$$

$$d\bar{G}^L = d\bar{G}^V$$

Constant \bar{G}

$$V^L dP^{sat} - S^L dT = V^V dP^{sat} - S^V dT$$

$$\frac{dP^{sat}}{dT} = \frac{S^V - S^L}{V^V - V^L} = \frac{\Delta S^{V-L}}{\Delta V^{V-L}}$$

Using $\Delta \bar{G}^{V-L} = \Delta H^{V-L} - T\Delta S^{V-L} = 0$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{V-L}}{T\Delta V^{V-L}}$$

Clapeyron Eqn

Using

$$\Delta V^{V-L} = V^V - V^L \approx V^V$$

* Volume of vapour is bigger than volume of liquid

Approximation: Low pressure (ideal gas)

$$\Delta V^{V-L} \approx V^V = \frac{RT}{P^{sat}}$$

If we substitute on Clapeyron:

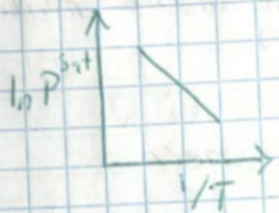
We use

$$\Delta H^{V-L} = \frac{T^2 R}{P^{sat}} \frac{dP^{sat}}{dT} = R \frac{d \ln P^{sat}}{\left(\frac{1}{T}\right) dT}$$

$$d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT$$

$$\Delta H^{V-L} = -R \frac{d \ln P^{sat}}{d\left(\frac{1}{T}\right)} \quad \left. \vphantom{\Delta H^{V-L}} \right\} \text{Clausius-Clapeyron}$$

If we plot $\ln P^{sat}$ vs $1/T$



This suggest:

$$\ln P^{sat} = A - \frac{B}{T}$$

Antoine

$$\ln P^{sat} = A - \frac{B}{T+C}$$

G → Capital is for total System

g → Lower is for molar (single component)

SINGLE PHASE, CLOSED SYSTEM

per mol: $dg = v dP - s dT$

$$n_t g = G$$

Total: $dG = V dP - S dT$

$$d(n_t g) = (n_t v) dP - (n_t s) dT$$

$$\left. \frac{\partial (n_t g)}{\partial P} \right|_T = n_t v \quad ; \quad \left. \frac{\partial (n_t g)}{\partial T} \right|_P = -n_t s$$

OPEN SYSTEM, SINGLE PHASE, MULTICOMPONENT

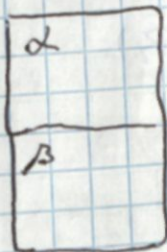
$$n_t = n_1 + n_2 + \dots + n_m = \sum_{i=1}^m n_i$$

$$n_t g = f(T, P, n_1, n_2, \dots, n_m)$$

$$d(n_t g) = \left. \frac{\partial (n_t g)}{\partial T} \right|_{P, n_i} dT + \left. \frac{\partial (n_t g)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial (n_t g)}{\partial n_1} \right|_{P, T, n_{j \neq 1}} dn_1 + \left. \frac{\partial (n_t g)}{\partial n_2} \right|_{P, T, n_{j \neq 2}} dn_2 + \dots$$

$$\mu_i = \left. \frac{\partial (n_t g)}{\partial n_i} \right|_{P, T, n_{j \neq i}} \rightarrow \text{Chemical Potential of } i$$

Constant T, P For each phase



$$T^\alpha = T^\beta$$

$$\mu_i^\alpha = \mu_i^\beta$$

$$P^\alpha = P^\beta$$

$$d(n_t g)^\alpha = (n_t v)^\alpha dP - (n_t s)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$d(n_t g)^\beta = (n_t v)^\beta dP - (n_t s)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$$

we add both

$$d(n_t g)^\alpha + d(n_t g)^\beta = d(n_t g) = (n_t v) dP - (n_t s) dT + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

↓
Entire system

The closed system allow us to do

$$d(n_t g) = (n_t v) dP - (n_t s) dT = 0 \quad * \text{ No change in the number of moles}$$

Thus:

$$\sum_i \mu_i^\alpha d n_i^\alpha = - \sum_i \mu_i^\beta d n_i^\beta \rightarrow \text{Esta la escribi yo me lo}$$

$$\left. \begin{aligned} \sum_i (\mu_i^\alpha - \mu_i^\beta) d n_i^\alpha &= 0 \\ \mu_i^\alpha &= \mu_i^\beta \end{aligned} \right\} \text{ Estas se las rifó el profe}$$

* At equilibrium, Chemical potential is the same for both phases

Thermodynamic equilibrium is build by Thermal (Temperatures), Mechanical (Pressure) and Chemical (Potential) equilibrium

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Potencial químico es la tasa de cambio de la energía de Gibbs respecto a los moles en cada fase. No es muy útil porque no podemos medir la energía de Gibbs, entonces los ingenieros químicos optaron por:

Amagat's law: $V_t = \sum V_i = \sum \frac{n_i R T}{P_t} = \frac{R T}{P_t} \sum n_i = \frac{R T}{P_t} \sum n_i v_i$

$$P_t V_t = n_t R T \quad ; \quad P_t v = R T$$

Dalton's law: $P_t = \sum P_i$

For I.G. mixtures $M^{IG} = n_t m^{IG}$
↳ molar quantity

$$M^{IG}(T, P_t) = \sum n_i m_i^{IG}(T, P_i)$$

$$m^{IG}(T, P_t) = \sum y_i m_i^{IG}(T, P_i)$$

$$\begin{aligned} g^{IG}(T, P_t) &= \sum y_i g_i^{IG}(T, P_i) = \sum [y_i (T, P_i) - T S_i^{IG}(T, P_i)] \\ &= \sum y_i h_i^{IG}(T, P_i) - T \sum y_i S_i^{IG}(T, P_i) \end{aligned}$$

Homework: Show that for I.G. $h_i^{IG}(T, P_t) = h_i^{IG}(T, P_i)$
Entropy does not depend of pressure?

$$g^{IG}(T, P_t) = \sum y_i h_i^{IG}(T, P_t) - T \sum y_i S_i^{IG}(T, P_i)$$

$$dS^{IG} = \frac{C_p}{T} dT - \left(\frac{R}{P}\right) dP$$

$$\Delta S^{IG} = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) ; T = CTTE$$

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$$S_i^{IG}(T, P_t) - S_i^{IG}(T, P_i) = -R \ln \left(\frac{P_t}{P_i} \right) = -R \ln \left(\frac{P_t}{Y_i P_t} \right) = R \ln Y_i$$

$$g^{IG}(T, P_t) = \sum Y_i h_i^{IG}(T, P_t) - T \sum Y_i [S_i^{IG}(T, P_t) - R \ln Y_i]$$

$$= \sum Y_i [h_i^{IG}(T, P_t) - T S_i^{IG}(T, P_t)] + RT \sum Y_i \ln Y_i$$

$$g^{IG}(T, P_t) = \sum Y_i g_i^{IG}(T, P_t) + RT \sum Y_i \ln Y_i$$

$\sum Y_i \ln Y_i \rightarrow$ is known as the 'mixing term'

We now have an expression for Gibbs, let's work in another for Ch. Pote

$$G^{IG}(T, P_t) = n_t g^{IG}(T, P_t) = \sum n_i g_i^{IG}(T, P_t) + RT \sum n_i \ln Y_i ; Y_i = \frac{n_i}{n_t}$$

$$= \sum n_i g_i^{IG}(T, P_t) + RT \sum n_i \ln n_i - RT n_t \ln n_t$$

We use:

$$\mu_i^{IG} = \left. \frac{\partial (n_t g^{IG})}{\partial n_i} \right|_{P, T, n_j \neq i} = \frac{\partial}{\partial n_i} \left[\sum n_i g_i(T, P_t) \right]_{P, T, n_j \neq i} + \dots$$

$$= g_i(T, P_t) + RT \left[n_i \frac{\partial \ln(n_i)}{\partial n_i} + \ln(n_i) \right] - RT \left[n_t \frac{\partial \ln(n_t)}{\partial n_i} + \ln(n_t) \frac{\partial n_t}{\partial n_i} \right]$$

$$= g_i(T, P_t) + RT(1 + \ln(n_i)) - RT(1 + \ln(n_t)) ; Y_i = n_i / n_t$$

$$\mu_i^{IG} = g_i^{IG}(T, P_t) + RT \ln(Y_i)$$

↑
IG Mixture

$$\mu_i^V = \mu_i^L$$

→ Ideal mixture

↓
Similar chemistry (interactions)
Similar size

$$V^{ID} = \sum X_i V_i^L(T, P_t)$$

$$h^{ID}(T, P_t) = \sum X_i h_i^L(T, P_t)$$

$$S^{ID}(T, P_t) = \sum X_i S_i^L(T, P_t) - R \sum X_i \ln X_i$$

$$g^{ID}(T, P_t) = \sum X_i g_i^L(T, P_t) + RT \sum X_i \ln X_i$$

$$\mu^{ID}(T, P_t) = g_i^L(T, P_t) + RT \ln X_i$$

$$\mu_i^{IG}(T, P_t) = \mu_i^D(T, P_t)$$

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$$g_i^{IG}(T, P_t) + RT \ln Y_i = g^L(T, P_t) + RT \ln X_i$$

$$RT \ln \left(\frac{Y_i}{X_i} \right) = g^L(T, P_t) - g_i^{IG}(T, P_t)$$

Easy to measure

Hard to measure

We work with approximations: $g^L(T, P_t) \approx g^L(T, P^{sat})$

* Properties are insensitive to pressure in liquid phase

~~Approximation 1~~ $dg = v dP - s dT$ for constant T

Approximation 2: Vapor phase behaves as an ideal gas

$$dg^{IG} = V^{IG} dP = \frac{RT}{P} dP$$

$$g_i^{IG}(T, P_i^{sat}) - g_i(T, P_t) = \int_{P_t}^{P_i^{sat}} \frac{RT}{P} dP = RT \ln \left(\frac{P_i^{sat}}{P_t} \right)$$

Now we can substitute

$$RT \ln \left(\frac{Y_i}{X_i} \right) = \underbrace{g^L(T, P_i^{sat}) - g_i^{IG}(T, P_i^{sat})}_{=0} + RT \ln \left(\frac{P_i^{sat}}{P_t} \right)$$

Same conditions, we are in saturation, which means they both are the same

$$\ln \left(\frac{Y_i}{X_i} \right) = \ln \left(\frac{P_i^{sat}}{P_t} \right)$$

$$Y_i P_t = X_i P_i^{sat} \quad \text{Raoult's Law}$$

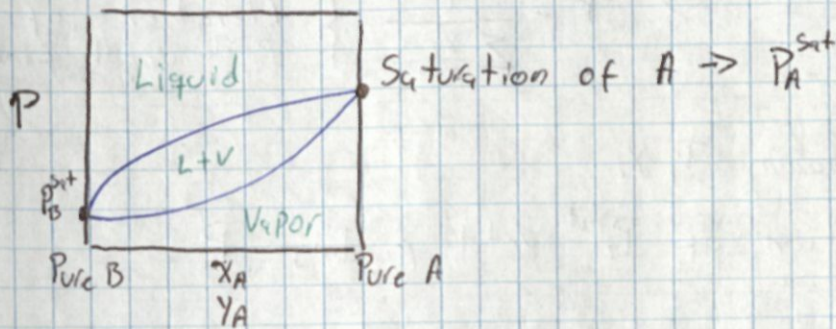
Assumptions // Approximations

1. - I.G. mixture
2. - Ideal liquid mixture

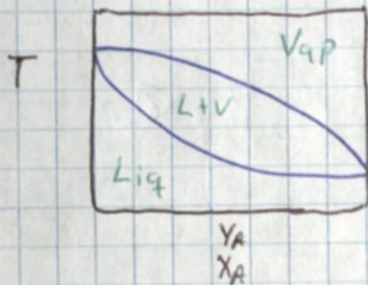
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VLE at constant Temperature

For a Binary Mixture



At constant Pressure



09/12/22

Raoult's Law: $y_i P = x_i P_i^{sat}$
 \downarrow
 P_t (Remember, Ideal GAs and Ideal mixture)

(A) Bubble Pressure (VLE) (Constant T)

Known: x_i, T Unknown: y_i, P $y_i P = x_i P_i^{sat}$

We have two unknown and 1 equation, so we use:

$$\sum y_i = 1$$

$$\sum y_i P = \sum x_i P_i^{sat} \Rightarrow P \sum y_i = \sum x_i P_i^{sat} \Rightarrow P = \sum x_i P_i^{sat}$$

(B) Dew Pressure (VLE) (Constant T)

Known: y_i, T Unknown: x_i, P

$$\sum x_i = 1 \Rightarrow 1 = \frac{y_i P}{P_i^{sat}} \Rightarrow \left(\sum \frac{y_i}{P_i^{sat}} \right)$$

(A) Bubble Dew Temperature (Constant P)

Known: P, y_i Unknown: T, x_i

$$\sum x_i = 1 \Rightarrow \sum \left(\frac{y_i P}{P_i^{sat}} \right) = 1 \Rightarrow P = \frac{1}{\sum \frac{y_i}{P_i^{sat}}} \left. \vphantom{\sum \left(\frac{y_i P}{P_i^{sat}} \right) = 1} \right\} \text{Iteration of } P_i^{sat} \text{ until find } P$$

(B) Bubble Temperature

Unknown: P, x_i Unknown: T, y_i

$$P = \sum x_i P_i^{sat} \rightarrow \text{Iteration of } P_i^{sat} \text{ until finding } P$$

REAL MIXTURES

$$y_i P = x_i P_i^{sat} \Rightarrow \phi_i y_i P = \gamma_i x_i P_i^{sat} \rightarrow \text{For real mixtures}$$

Raoult's Law

Ideal Gas
Ideal Mixture

Modified Raoult's Law

$$\begin{aligned} \gamma_i &= f(P, T, x_i) \rightarrow \text{Fugacity} \\ \phi_i &= f(P, T, y_i) \rightarrow \text{Activity?} \end{aligned}$$

FUGACITY

$$dg = v dP - s dT \rightarrow \text{Constant } T \rightarrow dg = v dP$$

Effect of P on g at constant T : $P^* \rightarrow P$

$$g - g^* = \int_{P^*}^P v dP$$

Let $P^* \rightarrow 0$ Thus $v^* \rightarrow 0$

$$\text{For an ideal gas we have } dg^{ig} = v dP = \frac{RT}{P} dP = RT d \ln(P)$$

We can define, for a real fluid:

$$dg = RT d \ln(f)$$

We can also write

$$g - g^{ig} = RT d \ln(f) - RT d \ln(P)$$

$$dg^R = RT d \ln \left(\frac{f}{P} \right) = RT d \ln(\phi)$$

$$g^R = g - g^{ig} = RT \ln(\phi) + C(T)$$

Consider Ideal Gas

$$g^R = g^{ig} - g^{ig} = 0$$

$$\phi = \frac{f}{P} = \frac{P}{P} = 1$$

$f \rightarrow$ Fugacity
 $\phi \rightarrow$ Fugacity coefficient

We can re-write:

$$g - g^{\text{sat}} = g = RT \ln(\phi) = RT \ln\left(\frac{f}{P}\right)$$

For a pure component i

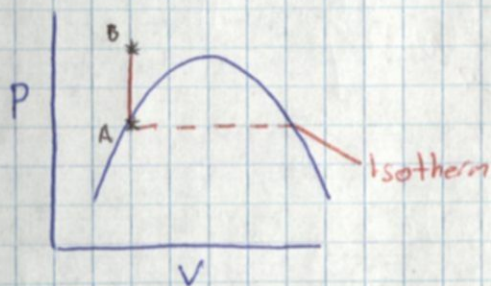
$$dg_i = RT d \ln(f_i)$$

Integrate from state of saturated liquid to saturated vapor.

$$g_i^{\text{sat},V}(T, P_i^{\text{sat}}) - g_i^{\text{sat},L}(T, P_i^{\text{sat}}) = RT \ln\left(\frac{f_i^{\text{sat},V}}{f_i^{\text{sat},L}}\right)$$

At saturation, $g^V = g^L$, which means that for VLE

$$f_i^{\text{sat},V} = f_i^{\text{sat},L}; \quad g_i^{\text{sat},V} = g_i^{\text{sat},L}; \quad \mu_i^{\text{sat},V} = \mu_i^{\text{sat},L}$$



* Vamos a encontrar una expresión para fugacidad fuera del punto de saturación.

* Isotherm has three slopes

We start with

$$dg_i = RT d \ln(f_i) = \underbrace{V_i^L dP}_{\text{Constant } T} \Rightarrow d \ln(f_i) = \left(\frac{V_i^L}{RT}\right) dP$$

$$\ln\left(\frac{f_i^L(P)}{f_i^L(P_i^{\text{sat}})}\right) = \frac{1}{RT} \int_{P_i^{\text{sat}}}^P V_i^L dP$$

* We can not integrate for liquid so we make an approximation of $V_i^L \approx \text{Constant}$

$$= \frac{V_i^L}{RT} (P_i - P_i^{\text{sat}})$$

$$f_i^L(P) = f_i^L(P_i^{\text{sat}}) e^{\left[\frac{V_i^L}{RT} (P_i - P_i^{\text{sat}})\right]}$$

* We can not measure f_i^L , but we can remember $f_i^L = f_i^V$ at saturation

$$f_i^L(P) = f_i^V(P_i^{\text{sat}}) e^{\left[\frac{V_i^L}{RT} (P_i - P_i^{\text{sat}})\right]}$$

$$f_i^L(P) = \phi_i^{\text{sat}} P_i^{\text{sat}} e^{\left[\frac{V_i^L}{RT} (P_i - P_i^{\text{sat}})\right]} \quad \left. \vphantom{f_i^L(P)} \right\} \text{Poynting}$$

The exponent will be ≈ 1 unless Pressure is incredible high

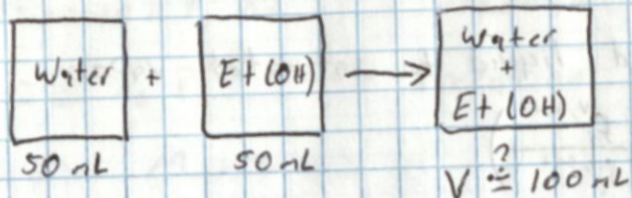
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And $\phi_i \approx 1$ usually

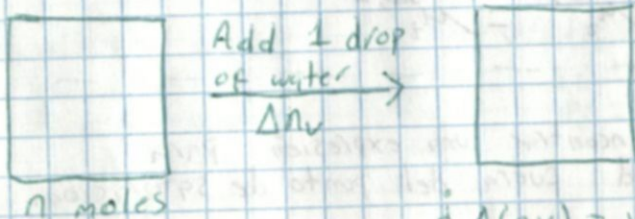
The exponent is the 'Poynting correction factor'

MIXTURES

* The real volume is < 100 mL
Volumes are not additive



Water + EtOH Mixture



molar volume = v

$\Delta(nv) = V_w \Delta n_w$? No!

$\Delta(nv) = V_w^{eff} \Delta n_w$

$V = nv$

Total volume

$V_w^{eff} = \frac{\Delta(nv)}{\Delta n_w} = \frac{\partial(nv)}{\partial n_w} \Big|_{P, T, n_{EtOH}}$

Partial molar properties

PARTIAL MOLAR PROPERTIES

Property m :

$\bar{m}_i = \frac{\partial(n_m)}{\partial n_i} \Big|_{P, T, n_{j \neq i}}$

Property Gibbs

$\bar{g}_i = \frac{\partial(n_g)}{\partial n_i} \Big|_{P, T, n_{j \neq i}} = \mu_i$

Entropy

$\bar{h}_i = \frac{\partial(n_h)}{\partial n_i} \Big|_{P, T, n_{j \neq i}}$

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For ideal mixtures

$$m = \sum x_i m_i$$

↗ * Esto es verdad, excepto para S y G

For real mixtures

$$m = \sum x_i \bar{m}_i$$

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Partial molar properties

Quiz 1: 09/21

$$\bar{m}_i = \left. \frac{\partial (n_t m)}{\partial n_i} \right|_{P, T, n_{j \neq i}}$$

$$M = n_t m$$

$$d(n_t m) = \left. \frac{\partial (n_t m)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial (n_t m)}{\partial T} \right|_{P, n_i} dT + \sum_i \left. \frac{\partial (n_t m)}{\partial n_i} \right|_{P, T, n_{j \neq i}} dn_i$$

$$d(n_t m) = \left. \frac{\partial (n_t m)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial (n_t m)}{\partial T} \right|_{P, n_i} dT + \sum \bar{m}_i dn_i \quad (1)$$

$$d(n_t m) = n_t dm + m dn_t \quad (2)$$

$$dn_i = d(x_i n_t) = x_i dn_t + n_t dx_i \quad (3)$$

$$n_i dm + n_i dn_t = n_t \left(\frac{\partial m}{\partial P} \right) dP + n_t \left(\frac{\partial m}{\partial T} \right) dT + \sum \bar{m}_i (x_i dn_t + n_t dx_i)$$

$$\left[dm - \left(\frac{\partial m}{\partial P} \right) dP - \left(\frac{\partial m}{\partial T} \right) dT - \sum \bar{m}_i dx_i \right] n_t + \left(m - \sum x_i \bar{m}_i \right) dn_t = 0$$

$$\left(dm - \left(\frac{\partial m}{\partial P} \right) dP - \left(\frac{\partial m}{\partial T} \right) dT - \sum \bar{m}_i dx_i \right) = 0$$

$$m = \sum x_i \bar{m}_i \Rightarrow dm = \sum x_i d\bar{m}_i + \sum \bar{m}_i dx_i$$

$$\sum x_i d\bar{m}_i + \sum \bar{m}_i dx_i - \left(\frac{\partial m}{\partial P} \right) dP - \left(\frac{\partial m}{\partial T} \right) dT - \sum \bar{m}_i dx_i = 0$$

At constant T and P we have left

$$\sum_i x_i d\bar{m}_i = 0$$

$$m = g = \bar{g}_i = \mu_i$$

$$\sum_i x_i d\mu_i = 0 \rightarrow \text{Gibbs Duhem Equation}$$

FUGACITY

For a Pure Fluid:

$$dg_i = RT d \ln(f_i) \Rightarrow d\mu_{i,pure} = RT d \ln(f_{i,pure})$$

Mixture:

$$d\mu = RT d \ln(\hat{f}_i) \quad \text{Definition}$$

* Homework: Show that for a pure fluid $g = \mu$ or $g_{i,pure} = \mu_{i,pure}$ * ~~Also~~ Hat over specific property (\hat{f}_i) means 'in a mixture'

EQUILIBRIUM CRITERIA

$$\text{Multicomponent VLE: } \mu_i^L = \mu_i^V, \quad d\mu_i^V = RT d \ln(\hat{f}_i^V)$$

$$d\mu_i^L = RT d \ln(\hat{f}_i^L)$$

Integrate from state of pure i to the mixture

$$\mu_i^V - \mu_{i,pure}^V = RT \ln \left(\frac{\hat{f}_i^V}{f_{i,pure}^V} \right) \quad (A)$$

$$\mu_i^L - \mu_{i,pure}^L = RT \ln \left(\frac{\hat{f}_i^L}{f_{i,pure}^L} \right) \quad (B)$$

We do A-B and: For VLE of pure i $\mu_{i,pure}^V = \mu_{i,pure}^L$

$$f_{i,pure}^V = f_{i,pure}^L$$

$$RT \ln \left(\frac{\hat{f}_i^V}{f_{i,pure}^V} \right) = 0 \Rightarrow \hat{f}_i^V = f_{i,pure}^L \rightarrow \text{At equilibrium only (VLE)}$$

LIQUID PHASE 'ACTIVITY'

$$a_i = \frac{\hat{f}_i}{f_{i,pure}^L}$$

 $f_{i,pure}^L \rightarrow$ Zero stands for: Same T and P that the mixture

$$\hat{f}_i = \gamma_i x_i f_{i,pure}^L$$

 $\gamma_i \rightarrow$ Activity Coefficient

$$a_i = \gamma_i x_i$$

$$\hat{f}_i^V = \hat{f}_i^L = \gamma_i x_i f_{i,pure}^L$$

$$\hat{\phi}_i \gamma_i P = \gamma_i x_i f_{i,pure}^L$$

EXCESS PROPERTIES

For a property M in solution: $M^E = M - M^{ID}$

$$V^E = V - V^{ID} = V - \sum n_i v_i$$

Let $\bar{V}_i^E = \left. \frac{\partial (n_i V^E)}{\partial n_i} \right|_{P, T, n_{j \neq i}} \}$ Partial molar excess volume

g^E and γ_i are related

$$g^E = g - g^{IG} = (g - \sum x_i g_i) - (g^{ID} - \sum x_i g_i)$$

$$= \Delta g_{mix} - RT \sum x_i \ln(x_i)$$

Recalling $g^{ID} = \sum x_i g_i + RT \sum x_i \ln(x_i)$

$$\Delta g_{mix} = g - \sum x_i g_i, \text{ recalling } m = \sum x_i \bar{m}_i$$

$$= \sum x_i \bar{g}_i - \sum x_i g_i, \text{ recalling } \bar{g}_i = \mu_i$$

$$= \sum x_i \mu_i - \sum x_i g_i = \sum (x_i)(\mu_i - g_i)$$

$$\Delta g_{mix} = RT \sum x_i \ln \left(\frac{\hat{f}_i}{f_{i, pure}^0} \right) = RT \sum x_i \ln(\gamma_i x_i)$$

$$g^E = RT \sum x_i \ln(\gamma_i x_i) - RT \sum x_i \ln(x_i)$$

$$g^E = RT \sum x_i \ln(\gamma_i)$$

$$\frac{g^E}{RT} = \sum x_i \ln(\gamma_i) = \sum x_i \left(\frac{\bar{g}_i^E}{RT} \right) \Rightarrow RT \ln(\gamma_i) = \bar{g}_i^E$$

VLE of a mixture

$$\hat{f}_i^v = \hat{f}_i^L$$

$$\underbrace{\hat{\Phi}_i y_i P}_{\text{Vapor}} = \underbrace{\gamma_i x_i f_{i, pure}^0}_{\text{Liquid}}$$

Liquid $f_{i, pure}^0 = \phi_i^{sat} P_i^{sat} \exp \left[\frac{v_i^L (P - P_i^{sat})}{RT} \right]$

For Low to moderate Pressures

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$$\phi_i^v \approx 1, \phi_i^{sat} \approx 1, \exp[\dots] \approx 1$$

So we have

$$f_{i,pure} \approx P_i^{sat}$$

$$y_i P = \gamma_i x_i P_i^{sat} \rightarrow \text{Modified Raoult's Law}$$

Binary Mixture, Low to moderate pressure

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

$$\lim_{x_i \rightarrow 1} \gamma_i = \lim_{x_i \rightarrow 1} \frac{y_i P}{x_i P_i^{sat}} = \frac{P_i^{sat}}{P_i^{sat}} = 1$$

$$\lim_{x_i \rightarrow 1} \ln(\gamma_i) = 0$$

Slope at $x_i \rightarrow 1$

$$\lim_{x_i \rightarrow 1} \frac{d \ln(\gamma_i)}{dx_i} = d?$$

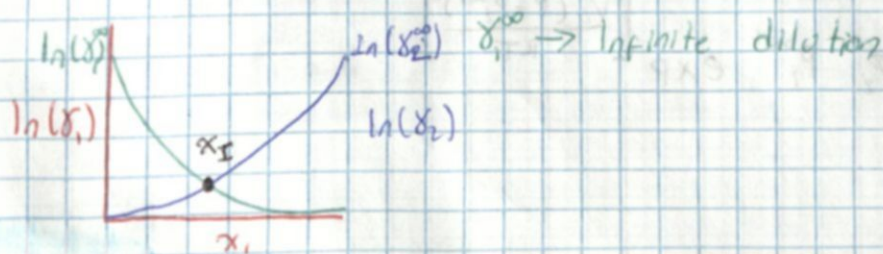
γ_i está asociado a \bar{g}^E , entonces usamos la relación de Gibbs Duhem

$$\sum x_i d \ln(\gamma_i) = 0$$

$$x_1 \frac{d \ln(\gamma_1)}{dx_1} + x_2 \frac{d \ln(\gamma_2)}{dx_2} = 0$$

$$\lim_{x_1 \rightarrow 1} \frac{d \ln(\gamma_1)}{dx_1} = \lim_{x_1 \rightarrow 1} \left(\frac{x_2}{x_1} \right) \frac{d \ln(\gamma_2)}{dx_2} = 0$$

$\lim_{x_1 \rightarrow 0} \gamma_1 = \gamma_1^\infty \rightarrow$ Infinite dilution activity coefficient



$$\frac{g^E}{RT} \text{ vs } x_i$$

$$\frac{g^E}{RT} = \sum x_i \ln(\gamma_i) = \sum x_i \left(\frac{g_i^E}{RT} \right)$$

For binary mixture

$$\frac{g^E}{RT} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2)$$

$$\lim_{x_1 \rightarrow 0} \left(\frac{g^E}{RT} \right) = \underbrace{0 \ln(\gamma_1)}_0 + \underbrace{1 \ln(\gamma_2)}_0 \quad \therefore \lim_{x_1 \rightarrow 0} \left(\frac{g^E}{RT} \right) = 0$$

$$\text{Also } \lim_{x_1 \rightarrow 1} \left(\frac{g^E}{RT} \right) = 0$$

• What is the value of $\left(\frac{g^E}{RT} \right)$ when both lines meet? (x_I)

$$\text{at } x_1 = x_I, \quad \ln(\gamma_1) = \ln(\gamma_2), \quad \gamma_1 = \gamma_2$$

$$\frac{g^E}{RT} = x_1 \ln(\gamma_1) + (1-x_1) \ln(\gamma_1)$$

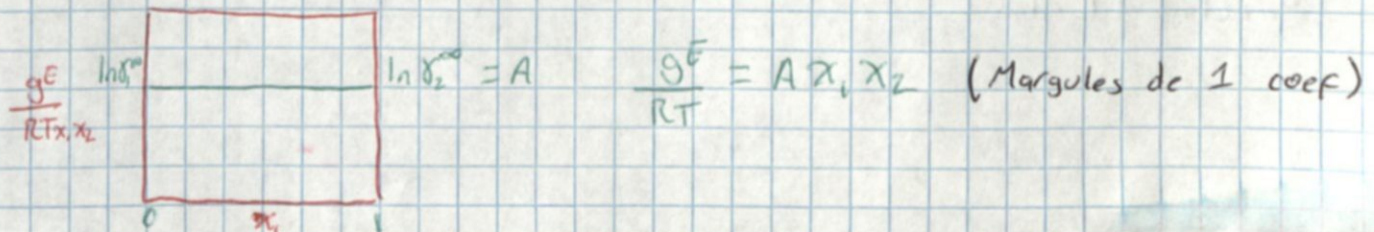
$$\left(\frac{g^E}{RT} \right) = \ln \gamma_1 = \ln \gamma_2 \quad \text{at } x_1 = x_I$$

$$\lim_{x_1 \rightarrow 0} \frac{g^E}{RT x_1 x_2} = \lim_{x_1 \rightarrow 0} \frac{(g^E/RT)}{x_1 x_2} = \frac{0}{0} \rightarrow \text{We need L'Hopital's rule}$$

$$\begin{aligned} \lim_{x_1 \rightarrow 0} \left[\frac{\frac{d}{dx_1} \left(\frac{g^E}{RT} \right)}{\frac{d}{dx_1} (x_1 x_2)} \right] &\Rightarrow \lim_{x_1 \rightarrow 0} \frac{d}{dx_1} \left(\frac{g^E}{RT} \right) = \lim_{x_1 \rightarrow 0} \frac{d}{dx_1} (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \\ &= \ln \gamma_1 + x_1 \frac{d \ln(\gamma_1)}{dx_1} - \ln \gamma_2 + x_2 \frac{d \ln \gamma_2}{dx_1} \\ &= \ln \gamma_1 - \ln \gamma_2 \Big|_{\lim_{x_1 \rightarrow 0}} = \ln \gamma_1^\infty - \underbrace{\ln(1)}_0 = \ln \gamma_1^\infty \end{aligned}$$

Simplest case

$$\text{Let } \gamma_1^\infty = \gamma_2^\infty \quad \text{and} \quad \frac{g^E}{RT x_1 x_2} = \ln \gamma_1^\infty = \ln \gamma_2^\infty = A$$



Redlich Kister Model

$$\frac{g^E}{RTx_1x_2} = B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \dots$$

$Y_i P = \gamma_i x_i P_i^{sat}$, we have Margule's one parameter model: $\frac{g^E}{RT} = A x_1 x_2$

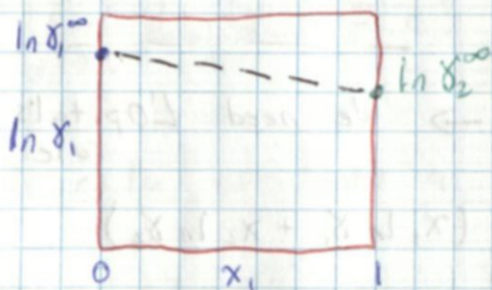
Let's find $\ln \gamma_i$

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = \frac{\sum x_i \ln \gamma_i}{\sum x_i \left(\frac{g_i^E}{RT} \right)}$$

$$\ln \gamma_1 = \frac{\partial}{\partial n_1} \left(\frac{n_1 g^E}{RT} \right)_{P,T,n_2} = \frac{\partial}{\partial n_1} \left[\frac{n_1 A \left(\frac{n_1}{n_1+n_2} \right) \left(\frac{n_2}{n_1+n_2} \right) \right]_{P,T,n_2} = \frac{\partial}{\partial n_1} \left(\frac{A n_1 n_2}{n_1+n_2} \right)_{P,T,n_2}$$

$$= A n_2 \frac{\partial}{\partial n_1} \left(\frac{n_1}{n_1+n_2} \right)_{P,T,n_2} = A x_2^2 \rightarrow \text{Ahorita la intento}$$

And for $\ln \gamma_2 = A x_1^2$

Margule's Two Parameter Model

$\ln \gamma_1^\infty \neq \ln \gamma_2^\infty$ but $\frac{g^E}{RTx_1x_2}$ vs x_1 is a straight line

$$\frac{g^E}{RTx_1x_2} = (A_{21} - A_{12}) x_1 + A_{12}$$

$$\frac{g^E}{RT} = x_1 x_2 [(A_{21} x_1 + A_{12} x_1) + A_{12}]$$

* Homework: Show that $\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1]$
 $\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$

To understand the physical meaning let's do:

$$\lim_{x_1 \rightarrow 0} \ln \gamma_1 = \ln \gamma_1^\infty = A_{12} \quad \lim_{x_2 \rightarrow 0} \ln \gamma_2 = \ln \gamma_2^\infty = A_{21}$$

* Estos modelos estan relacionados con los coeficientes de actividad de mezclas diluidas

Van Laar

Assumption

$$g^E = h^E + Ts^E$$

$$\left. \begin{array}{l} v^E = 0 \\ s^E = 0 \end{array} \right\} \text{Regular Solutions}$$

$$g^E = u^E + \underbrace{PV^E}_0 - \underbrace{Ts^E}_0 \Rightarrow g^E = u^E$$

$$\frac{g^E}{RT} = \frac{u^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})} \rightarrow \text{Jumping lots of steps}$$

$$\ln \gamma_1 = \frac{\partial}{\partial n_1} \left(n_t \frac{g^E}{RT} \right)_{T, P, n_2} = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2} \right]^2} \quad \int \frac{A_{21}}{\left[1 + \frac{A_{21} x_2}{A_{12} x_1} \right]^2}$$

If we do

$$\lim_{x_1 \rightarrow 0} \ln \gamma_1 = \ln \gamma_1^\infty = A_{12} \quad \text{and} \quad \lim_{x_2 \rightarrow 0} \ln \gamma_2 = \ln \gamma_2^\infty = A_{21}$$

SCATCHARD AND HILDEBRAND THEORY.

09/21/22

$$v^E = 0, \quad s^E = 0$$

$$g^E = u^E = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 (x_1 v_1 + x_2 v_2)$$

Volume fraction

Solubility parameter

* Look at the parameters.
It will always be positive

$$(g^E) \quad g^E > 0$$

If $\delta_1 \approx \delta_2 \rightarrow g^E \approx 0$ And behaves as ideal mixture

$$RT \ln \gamma_1 = v_1 \phi_2^2 (\delta_1 - \delta_2)^2, \quad \text{again, if } \delta_2 \approx \delta_1 \rightarrow \gamma_1 \approx 1$$

FLORY HUGGINS MODEL

$$g^E = h^E - Ts^E = u^E + PV^E - Ts^E$$

This model says that for polymer solutions where packing is so important

$$g^E = v^E + PV^E - Ts^E = RT \left[x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \right]$$

1. - Solvent
2. - Polymer

Lattice model

Polymer
 Solvent

$$S = k_B \ln w$$

\downarrow
 Boltzmann

\downarrow
 Number of configurations

$$\phi_2 = 7/25, \quad x_2 = 1/19$$

$$g^E = h^E + RT \left[x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \right]$$

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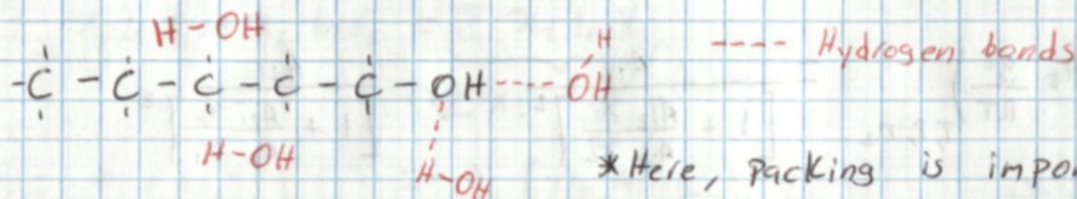
$$h^E = \phi_1 \phi_2 (x_1 + r x_2) \chi RT$$

χ : Strength of interaction

If $\chi = 0 \rightarrow g^E = RT [x_1 \ln \dots]$

We have an Athermal solution

LOCAL COMPOSITION THEORIES: PRAUSNITZ



* Here, packing is important

Wilson Model

$$\frac{g^E}{RT} = - \sum_j x_j \ln \left(\sum_i x_i \Lambda_{ji} \right), \quad \Lambda_{ji} = \frac{V_i}{V_j} \exp \left(\frac{-A_{ji}}{RT} \right)$$

Parameters

$-A_{ji}$ is interaction parameter

* Everything comes w/ interactions and packing

If you diferenciamos

$$\ln \gamma_k = 1 - \ln \left(\sum_i x_i \Lambda_{ki} \right) - \sum_j \frac{x_j \Lambda_{jk}}{\sum_i x_i \Lambda_{ji}}$$

For a binary mixture

$$\ln \gamma_1 = - \ln (x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right)$$

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QUIZ 2: 10/05

MIDTERM 1: 10/12

Non Random Two Liquid (NRTL) Model

$$\left(\frac{g^E}{RT} \right) = x_1 x_2 \left[\frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} + \frac{\tau_{21} G_{21}}{x_2 + x_1 G_{21}} \right] \quad \text{Where} \quad \ln G_{12} = -\alpha \tau_{12}$$

$$\ln G_{21} = -\alpha \tau_{21}$$

Parameters: α, G_{12}, G_{21}

and $G_{ij} \neq n_i g$ (Not Gibbs energy)

$\alpha = \frac{1}{z}$ Coordination number

* Normalmente $6 < \alpha < 14$

$1/\rho \propto \rightarrow 0$

$\frac{g^E}{RT} = x_1 x_2 (\tau_{21} + \tau_{12}) \rightarrow \underbrace{x_1 x_2 A}_{\text{Margule's model}}$

Homework \rightarrow Show that $\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \left(\frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right) \right]$
 from NRTL model

e-NRTL: Electrolyte systems

a-NRTL: Adsorption

UNIQUAC MODEL [Abraham & Prausnitz, 1975]

Statistical mechanics bases

$\frac{g^E}{RT} = \frac{g^E(\text{Combinatorial})}{RT} + \frac{g^E(\text{residual})}{RT}$

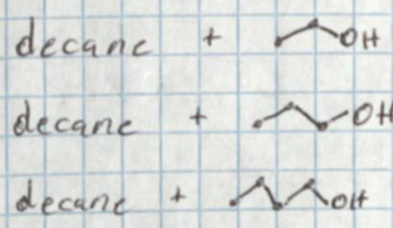
$\frac{g^E(\text{Combinatorial})}{RT} = \sum_i x_i \ln \left(\frac{\phi_i}{x_i} \right) + \left(\frac{z}{z} \right) \sum_i x_i q_i \ln \left(\frac{\theta_i}{\phi_i} \right)$
 (Note: z is labeled as coordination number)

$\frac{g^E(\text{Residual})}{RT} = \sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right)$

Where: $\phi_i = \text{Volume fraction of } i = \frac{x_i v_i}{\sum x_i v_i}$ \rightarrow Volume parameter of i
 $\theta_i = \text{Area fraction of } i = \frac{x_i q_i}{\sum x_i q_i}$ \rightarrow Area parameter of i

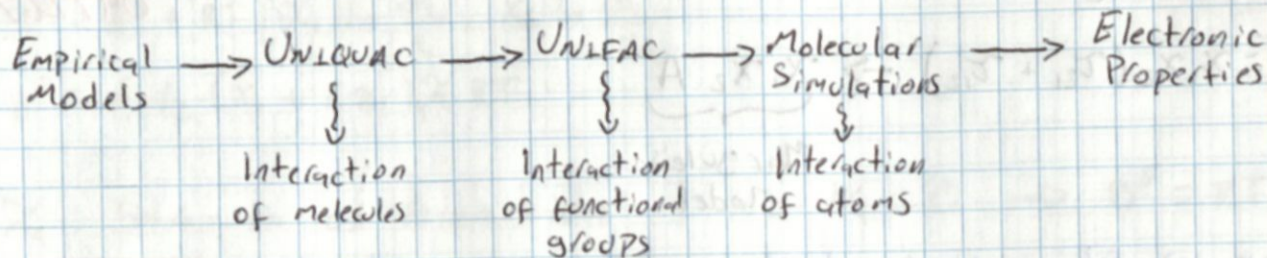
UNIFAC (Prausnitz, 1975)

* Universal function application? coefficient



* Para el modelo Uniquac se necesitan parámetros para cada componente molécula
 * Este modelo dice que los parámetros son para cada grupo funcional, no para cada componente molécula

09/26/22



INTERMOLECULAR INTERACTIONS

Ideal Gas: No interactions

Non-idealities: Due to interactions

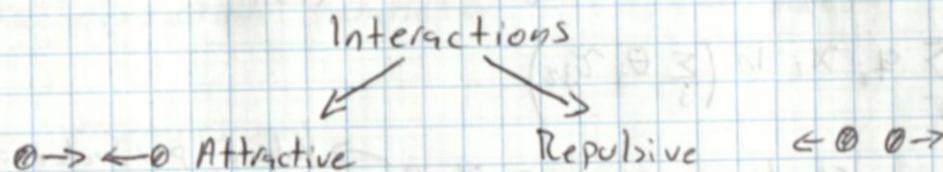
Mixtures of species A and B

Interactions: A-A, B-B, A-B (Relative strength is the one that matters)

U_{AA} U_{BB} U_{AB}

U_{ij} → Potential energy

* U → internal energy in classical thermo
 E → internal energy in statistical mechanics



Types of interactions

- 1) Electrostatic: Ions, ionic liquids, H-F
- 2) Induction: Between a charged species / permanent dipole and an induced dipole
- 3) Dispersion: Induced dipole - induce dipole
- 4) Specific forces

09/28/22

$$F = -\frac{\partial U}{\partial r}$$

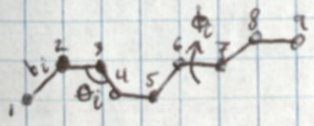
F : Force

U : Interactions (Potential energy)

r : Separation distance between atoms

$U = U(r)$ → Majority of times is only dependent of r

A simple example:



$$U_{1-9} = U(b_i, \theta_i, \phi_i)$$

* Depends on the representation

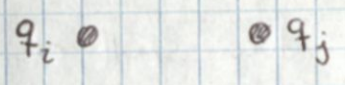
Approximation

$r_{ij} \rightarrow$ Distance between atom i and j

$$U_{\text{system}} = \sum_{i,j} U(r_{ij})$$

$$\sum_{i,j} = \sum_i \sum_{j>i}$$

1) Electrostatic: Due to point charges



$$U_{ij}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r}$$

as $r \rightarrow \infty$, $U_{ij} \rightarrow 0$ Thus Constant = 0

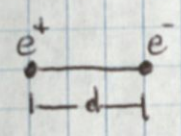
$$F_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r^2}$$

* The sign of U_{ij} tells if it's repulsive or attractive. (-) Attractive (+) Repulsive

** ENERGY SCALE $\sim RT \sim 0.6$ Kcal/mol at room temperature

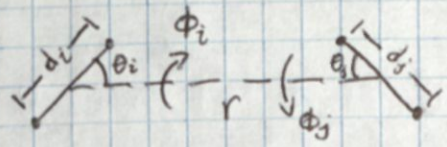
For 'Electrostatics' typically: tens of RT

Dipoles



$\mu = ed$ ~~coulombs meter~~ [coulombs-meter]
dipole moment

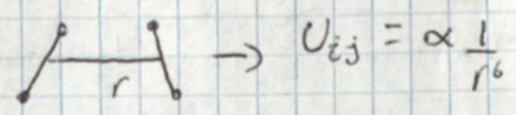
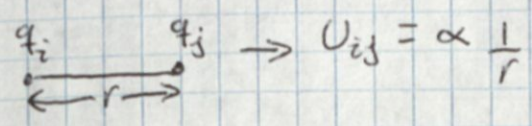
Φ : Torque



Here: $U_{ij} = \frac{-\mu_i \mu_j}{4\pi\epsilon_0 r^3}$ } Simplified for only r dependence

dipole-dipole
$$U_{ij}(r) = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon_0)^2 kT r^6}$$

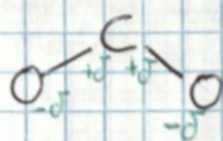
Comparing:



* Energy is way bigger for the first case

Quadrupole (4 Point charges) $\bar{U} \rightarrow$ Average

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For this case $\bar{U} = \frac{-\mu_i^2 Q_j}{(4\pi\epsilon_0)^2 K T r^8}$

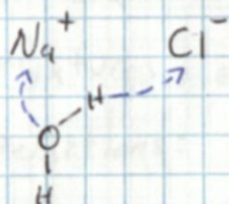
dipole-quadrupole

$$\bar{U}_{\text{quadrupole/quadrupole}} = \frac{-7 Q_i^2 Q_j^2}{40 (4\pi\epsilon_0)^2 K T r^{10}}$$

$$Q_i = \sum_i e_i d_i^2$$

$\text{NaCl} > \text{HF} > \text{CO} > \text{CO}_2$ \rightarrow We expect this

2) Induction Forces



* Strong charges (NaCl) will induce small charges on the other molecule (H_2O)

* Molecules that do not have permanent dipoles \Rightarrow Their structure is distorted in presence of strong charges/ions

Induced dipole moment

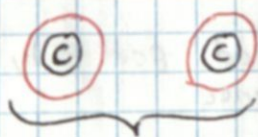
$$\mu^i = \alpha E$$

\downarrow Polarizability \rightarrow Electric field

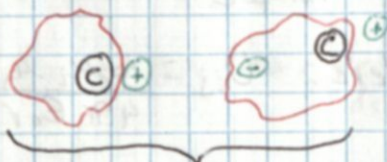
$$\bar{U}_{ij}(r) = \frac{-\alpha_i \mu_j^2}{(4\pi\epsilon_0)^2 r^6}$$

dipole-induced dipole

3) Dispersion forces (Van der Waals forces)



Idealization:
Same size, same geometry



Reality: a 'mini' dipole is created in each molecule

$$U_{ij} = -\frac{3}{2} \frac{\alpha_i \alpha_j}{(4\pi\epsilon_0)^2 r^6} \left[\frac{h\nu_{oi} h\nu_{oj}}{h\nu_{oi} + h\nu_{oj}} \right]$$

$\nu_{oi} \rightarrow$ Electronic frequencies

Don't worry about this one

$$\bar{U}_{ij}(r) = -\frac{3}{4} \frac{A}{(4\pi\epsilon_0)^2 r^6} = -\frac{B}{r^6} \rightarrow \text{Collection of constants}$$

Large distances it is attractive, but at small distances it must be repulsive.

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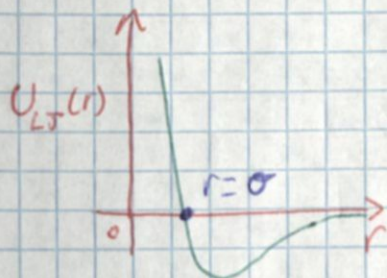
for large r for small r

$$U_{ij} \approx \propto \frac{1}{r^6}$$

$$U_{ij} \approx \frac{1}{r^{12}}$$

The Lennard-Jones

$$U_{LJ}(r) = 4E \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

 σ : Diameter of the atom

10/03/22

To find the minimum we derivate the expression

$$\left(\frac{\partial U}{\partial r}\right) = 0 \Rightarrow r_{min} = 2^{1/6} \sigma \approx 1.12 \sigma$$

$$\frac{d}{dr} \left[4E \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right) \right] = 4E \left(\frac{d}{dr} \left(\frac{\sigma}{r}\right)^{12} \right) \rightarrow \text{Try it myself}$$

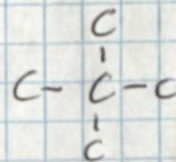
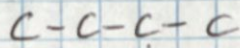
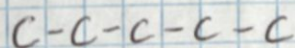
$$U_{min} = 4E \left[\left(\frac{\sigma}{1.12\sigma}\right)^{12} - \left(\frac{\sigma}{1.12\sigma}\right)^6 \right] \approx -E$$

* E is the maximum attraction $\sigma \rightarrow$ related to size, $E \rightarrow$ related to energy

n-pentane

iso-pentane

neo-pentane



Boiling Point 36°C

28°C

9.5°C

The packing is important. Molecular structure has important influence over interactions

4) Specific Interactions

Hydrogen bonding interactions

H_2O and CH_4 are pretty similar on size, number of atoms and molecular weight. But their boiling point is way to different ($100^\circ C$ for H_2O and around $-15^\circ C$ for CH_4). The reason for this is the hydrogen bonding

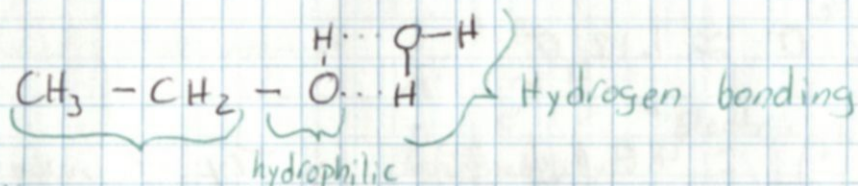
Quantitatively:

Strength of hydrogen bond $\approx 2 - 10$ kcal/mol

Strength of covalent bonding $\approx 50 - 100$ kcal/mol

Energy } Thermal energy ≈ 0.6 kcal/mol
Scale } at room temperature

Imagine an alcohol/water mixture



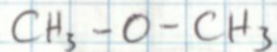
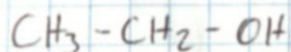
Hydrophobic

It is easier to form hydrogen bonds compared with modify the bonds (covalents)

Another example

Ethanol

Dimethyl ether



$78^\circ C$

$-25^\circ C$

\rightarrow Boiling Point

Electron acceptor — Electron donor

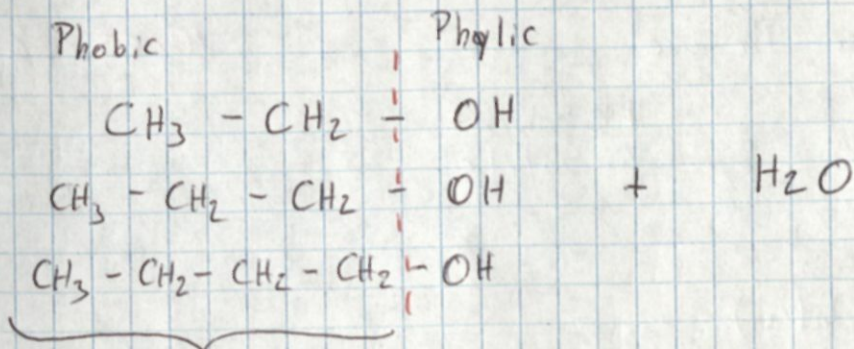
Trichloro-benzene

— Benzene

\downarrow
Electronegative

\downarrow
Pretty stable

Like to take electrons

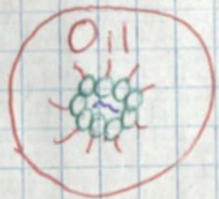


The hydrophobic part keeps gettin bigger and bigger



* The hydrophilic part is green
The hydrophobic part is red (hydrophobic core)
It is surrounded by water

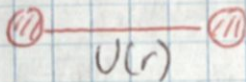
** This is a micelle



* The majority part is oil

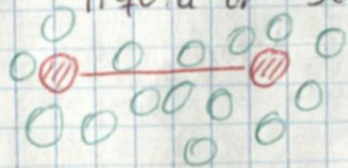
** This is a reverse-micelle

Interactions in gas phase



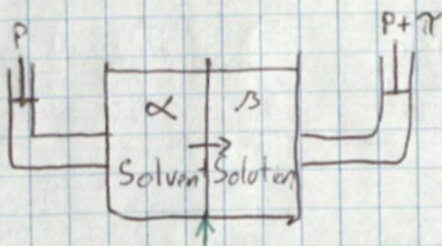
Lenard-Jones

Interactions in condensed phase liquid or solid



IT depends of it's surroundings
Potential of main force

OSMOTIC PRESSURE



Semi permeable membrane

Continuing with Osmotic Pressure

10/05/22

At Equilibrium

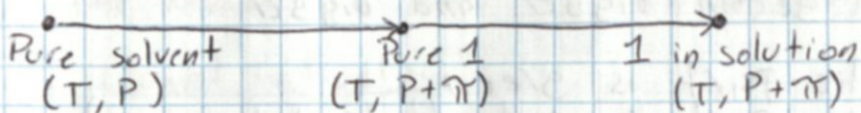
$$\mu_i^{\alpha} = \mu_i^{\beta}$$

1: Solvent

2: Solute

$$\mu_1^{\alpha} = \mu_{1, \text{pure}}^{\beta}(T, P)$$

$$\mu_2^{\alpha} = \mu_{2, \text{pure}}^{\beta}(T, P + \pi) + RT \ln(a_i)$$



$$dg_i = RT d \ln(f_i) \quad ; \quad d\mu_i = RT d \ln(\hat{f}_i) \quad \text{If we integrate}$$

$$\mu_{2, \text{soln}}^{\alpha}(T, P + \pi) - \mu_{2, \text{pure}}^{\beta}(T, P + \pi) = RT \ln \left(\underbrace{\frac{\hat{f}_2(T, P + \pi)}{f_2^{\circ}(T, P + \pi)}}_{a_i} \right) = RT \ln(a_i)$$

For Pure Solvent

$$\mu_{\text{pure } 1} = g_{\text{pure } 1}$$

$$dg = VdP - SdT \Rightarrow \left(\frac{\partial g}{\partial P} \right)_T = V \Rightarrow \left(\frac{\partial \mu}{\partial P} \right)_T = V$$

$$\left(\frac{\partial \mu_{\text{pure } 1}}{\partial P} \right)_T = V_{\text{pure } 1} \Rightarrow \mu_{\text{pure } 1}(T, P + \pi) = \mu_{\text{pure } 1}(T, P) + \pi V_{\text{pure } 1}$$

$$\mu_{\text{pure } 1}(T, P) = \mu_{\text{pure } 1}(T, P) + \pi V_{\text{pure } 1} + RT \ln a_i$$

$$\frac{\pi V_{\text{pure } 1}}{RT} = -\ln(a_i)$$

* We can not measure a_i as a direct variable so we need another relation

If we remember $a_i = \gamma_i x_i$

$$-\ln(\gamma_i x_i) = \frac{\pi V_{\text{pure } 1}}{RT}$$

$\gamma_i \rightarrow$ We have like 7 models to evaluate it

Approximations

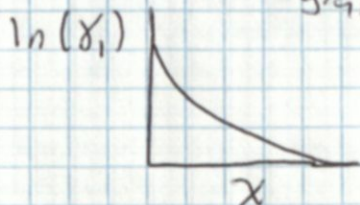
1) Solution is diluted

$$\text{Almost Pure 1} \rightarrow \gamma_i \approx 1$$

Thus

$$-\ln(x_i) = \frac{\pi V_{\text{pure } 1}}{RT}$$

* Remember this graph



2)

$$\ln(x_1) = \ln(1-x_2) \approx -x_2 - \frac{x_2^2}{2!} - \frac{x_2^3}{3!} - \dots$$

Since $x_2 \rightarrow 0$ (diluted) we discard all terms but the first

$$\ln(x_1) \approx -x_2$$

$$-\ln(x_1) = x_2 = \frac{\pi V_{\text{pure } 1}}{RT} \Rightarrow \frac{n_2}{(n_1+n_2)} = \frac{\pi V_{\text{pure } 1}}{RT}$$

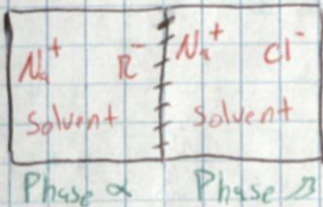
3) $\frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$ cuz' $n_1 \gg n_2$

$$\frac{n_2}{n_1} = \frac{\pi V_{\text{pure } 1}}{RT} \rightarrow n_2 RT = \pi(n_1 V_{\text{pure } 1})$$

4) $n_1 V_{\text{pure } 1} \approx$ Volume of the solution (Because we are diluted)

$$\pi V = n_2 RT \quad \text{Vant Hoff equation}$$

DONNAN EQUILIBRIUM



Semi permeable membrane
 Permeable for Na^+ , Cl^- , solvent
 Impermeable to R^-

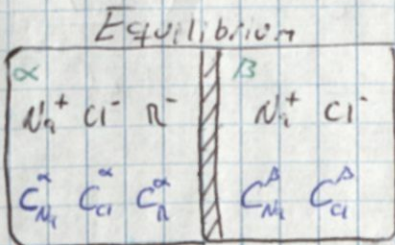
* We need to worry about electro something neutrality?

10/19/22

Class with the TA

1) Equality of chemical potential

2) Electroneutrality of both phases



Let's assume that δ represents the change in Na^+ concentration in α

$$\alpha: C_{\text{Na}}^{\text{f}\alpha} = C_{\text{Na}}^{\text{o}\alpha} + \delta \quad ; \quad C_{\text{Cl}}^{\text{f}\alpha} = C_{\text{Cl}}^{\text{o}\alpha} - \delta \quad ; \quad C_{\text{R}}^{\text{f}\alpha} = C_{\text{R}}^{\text{o}\alpha}$$

$$\beta: C_{\text{Na}}^{\text{f}\beta} = C_{\text{Na}}^{\text{o}\beta} - \delta \quad ; \quad C_{\text{Cl}}^{\text{f}\beta} = C_{\text{Cl}}^{\text{o}\beta} + \delta \quad ; \quad C_{\text{R}}^{\text{f}\beta} = 0$$

The goal is to find (calculate) the final equilibrium concentration in both sections i.e. calculate σ

Equality of solvent chemical potential

$$\mu_s^\alpha = \mu_s^\beta$$

$$\mu_s^\alpha = \mu_s^* + P^\alpha v_s + RT \ln(a_s^\alpha) \quad \mu_s^* \rightarrow \text{Standard state}$$

$$\mu_s^\beta = \mu_s^* + P^\beta v_s + RT \ln(a_s^\beta)$$

$$\frac{RT}{v_s} \ln \left[\frac{a_s^\beta}{a_s^\alpha} \right] = P^\alpha - P^\beta = \pi \rightarrow \text{Osmosis Pressure}$$

Equality of NaCl

NaCl exists as dissociated Na^+ and Cl^- ions

$$\mu_{\text{Na}}^\alpha + \mu_{\text{Cl}}^\alpha = \mu_{\text{Na}}^\beta + \mu_{\text{Cl}}^\beta \xrightarrow{\text{Conc to } \pi} \pi = \frac{RT}{(v_{\text{Na}} + v_{\text{Cl}})} \ln \left[\frac{a_{\text{Na}}^\beta a_{\text{Cl}}^\beta}{a_{\text{Na}}^\alpha a_{\text{Cl}}^\alpha} \right]$$

$$\mu_{\text{Na}}^* + P^\alpha v_{\text{Na}} + RT \ln(a_{\text{Na}}^\alpha) \rightarrow \text{with this here}$$

Assuming very diluted solution

$$a_s^\alpha = a_s^\beta = 1 \rightarrow a_{\text{Na}^+} \approx C_{\text{Na}^+} \quad \& \quad a_{\text{Cl}^-} \approx C_{\text{Cl}^-}$$

And our pressure expression becomes

$$\pi = \frac{RT}{v_s} \ln \left[\frac{1}{1} \right] = 0$$

$$C_{\text{Na}}^{\text{fa}} = C_{\text{Na}}^{\text{ox}} + \sigma \rightarrow (C_{\text{Na}}^{\text{fa}} + \sigma)\sigma - (C_{\text{Na}}^{\text{ox}} - \sigma)(C_{\text{Cl}}^{\text{ox}} - \sigma)$$

$$(C_{\text{Na}}^{\text{fa}} + \sigma)\sigma - (C_{\text{Na}}^{\text{ox}} - \sigma)^2 \rightarrow \sigma = \frac{(C_{\text{Na}}^{\text{ox}})^2}{C_{\text{Na}}^{\text{ox}} + 2C_{\text{Na}}^{\text{ox}}}$$

Thus

$$\pi = 2RT (C_{\text{Na}}^{\text{ox}} C_{\text{Na}}^{\text{ox}} + 2\sigma)$$

MOLECULAR THEORY OF CORRESPONDING STATES

- Stated by Van der Waals
- Macroscopic viewpoint: All substances show the same behavior in terms of the reduced properties. Substances at same reduced states are at 'corresponding state'

A universal Eqn of State (EOS) exist in terms of reduced properties

10/19/22

$$F\left(\frac{V}{V_c}, \frac{T}{T_c}, \frac{P}{P_c}\right) = 0; \quad T^* = \frac{T}{T_c}; \quad V^* = \frac{V}{V_c}; \quad P^* = \frac{P}{P_c}$$

Now, if we go for a microscopic viewpoint instead

Atoms have size (σ) and have characteristic 'interaction energy' (ϵ) associated with them

σ and ϵ can be used as characteristic length and energy scales of these atoms.

We can use reduced variables

$$T^* = \frac{KT}{\epsilon}; \quad V^* = \frac{V}{(N\sigma^3)} \quad P^* = \frac{P}{(\epsilon/\sigma^3)}$$

↓
Avogadro

Virtual Class

10/24/22

Math preliminaries

Variable assumes discrete values

u_1, u_2, \dots, u_n with probabilities $P(u_1), P(u_2), \dots, P(u_n)$

$$\text{Average value of } u = \bar{u} = \frac{\sum u_i P(u_i)}{\sum P(u_i)} = \sum u_i P(u_i)$$

The mean of a function of u

$$\overline{f(u)} = \sum f(u_i) P(u_i)$$

If u is a continuous variable and

$P(u) du$ = Probability that system is between u and $u + du$

$$\overline{f(u)} = \int_u f(u) P(u) du$$

Distribution of objects in states

N distinguishable objects

Number of ways of arranging these = $N(N-1)(N-2)\dots = N!$

10/24/22

Stirling Approximation

$$N! = (1)(2)(3)\dots(N)$$

$$\ln(N!) = \ln(1) + \ln(2) + \ln(3) + \dots + \ln(N) = \sum_{j=1}^N \ln(j)$$

$$\lim_{N \rightarrow \infty} \ln(N!) \approx N \ln(N) - N$$

Lagrange's Undetermined Multiplier Number

Find the maximum of function $f\{x_i\}$

Subject to constrain $g\{x_i\} = 0$

Finding maximum of $f\{x_i\} - \lambda g\{x_i\}$

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0$$

$$g\{x_i\} = 0$$

Same

~ Find maximum of product of moles fractions ~

$$f(x_1, x_2) = x_1 x_2$$

$$\text{Constrain } x_1 + x_2 = 1 \quad \text{or} \quad g(x_1, x_2) = x_1 + x_2 - 1 = 0$$

$$\frac{\partial f}{\partial x_1} = x_2$$

$$\frac{\partial g}{\partial x_1} = 1$$

$$\frac{\partial f}{\partial x_1} - \lambda \frac{\partial g}{\partial x_1} = x_2 - \lambda \rightarrow x_1 = \lambda$$

$$\frac{\partial f}{\partial x_2} = x_1$$

$$\frac{\partial g}{\partial x_2} = 1$$

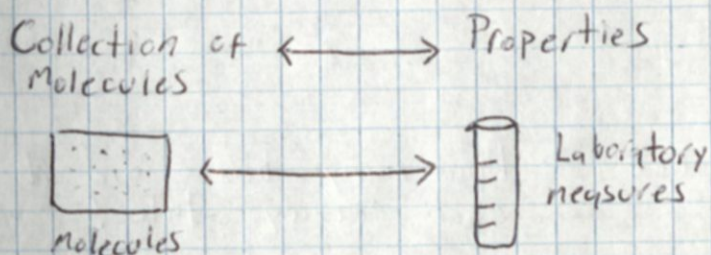
$$\frac{\partial f}{\partial x_2} - \lambda \frac{\partial g}{\partial x_2} = x_1 - \lambda \rightarrow x_2 = \lambda$$

$$x_1 = x_2 = \lambda$$

$$x_1 + x_2 - 1 = 0$$

$$\max f(x_1, x_2) = 0.25$$

10/26/22



ENSEMBLE



- 1) Create system replicas
- 2) Calculate property value for each replica
- 3) Calculate average value of property

Ensemble Average

Postulate: Ensemble average = Thermodynamic Property Value

Constant N, P, T : $dG = 0$ $dG \leq 0$ (Equilibrium)

Constant N, V, T : $dA = 0$ $dA \leq 0$ (Equilibrium)

CONSTANT	ENSEMBLE NAME	Extensive	Intensive
N, V, E	Microcanonical	N V E	μ P T
N, V, T	Canonical		
N, P, T	Isobaric, Isothermal		
μ, V, T	Grand Canonical		

* Se eligen 2 de un lado y 1 del otro, o las tres extensivas
 * Tambien se pueden elegir las 3 extensivas pero nunca las 3 intensivas

Most of the Thermodynamical properties come from the Canonical Ensemble

CANONICAL ENSEMBLE (N, V, T)

* We draw 9 boxes because space is a limitation

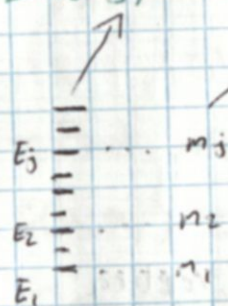


Constant N, V, T

Temperature T is fixed with a heat bath

T is constant, but E will change in each box
 \downarrow
 Can

Energy states



Occupation number \rightarrow How many boxes are at each energy state?

* The system is more likely to stay at lower energy

Two conditions

$$\sum_j m_j = \text{Total number} = M \quad (1)$$

of replicas

$$\sum_j m_j E_j = \bar{E} = \text{Total energy of the system} \quad (2)$$

$$W(\underline{m}) = \frac{M!}{m_1! m_2! m_3! \dots m_j! \dots} = \frac{M!}{\prod_k m_k!}$$

Many such that $W(\underline{m})$ distributions

$$P_j = \frac{\bar{m}_j}{M} \rightarrow \text{Average fraction of systems in } E_j \text{ or probability of finding systems in } E_j$$

For each we can calculate the number $\frac{m_j}{M} \rightarrow$ Fraction of systems that are in energy level E_j

$$P_j = \frac{1}{M} \left[\frac{\sum W(\underline{m}) m_j(\underline{m})}{\sum W(\underline{m})} \right]$$

CONSIDERATION: M is a VERY large number (i.e. 10^{25})

$$P_j \approx \frac{\bar{m}_j}{M}, \quad W(\underline{m}^*)$$

10/26/22

m_j^* = distribution that maximizes $W(\Omega)$

So we need to find the set $\{m_j^*\}$ that maximizes

$$W(\Omega) = \frac{M!}{\prod_k m_k!} \quad \text{subject to} \quad \sum m_j = M$$

$$\sum m_j E_j = E$$

Stirling: $\ln N! = N \ln N - N \dots$ when N is very large

Maximizing x is the same as maximizing $\ln(x)$

Maximizing $W(\Omega)$ is the same as maximizing $\ln W(\Omega)$

With Stirling:

$$\ln[W(\Omega)] = \frac{\ln N! + N}{N}$$

$$\ln W(\Omega) = \ln M! - \ln m_1! - \ln m_2! - \dots - \ln m_j! - \dots$$

$$= M \ln M - M - \left[\underset{-m_1}{m_1 \ln m_1} + \underset{-m_2}{m_2 \ln m_2} + \dots + m_j \ln m_j - m_j + \dots \right]$$

And $\sum_i m_i = M$

$$\ln W(\Omega) = M \ln(M) - \sum_k m_k \ln(m_k) \quad \text{to be maximized subject to}$$

To find the maximum

$$\frac{\partial}{\partial m_j} \left\{ \ln(W(\Omega)) - \alpha \sum_k m_k - \beta \sum_k m_k E_k \right\} = 0$$

Where α and β are undetermined multipliers

10/31/22

Quiz 3 11/09
midterm 2 11/16
Quiz 4 11/28

CANONICAL ENSEMBLE [Constant N, V, T]

$$P_j = \frac{m_j^*}{M}$$

$$\frac{\partial}{\partial m_j} \left\{ M \ln(M) - \sum_k m_k \ln(m_k) - \alpha \sum_k m_k - \beta \sum_k m_k E_k \right\} = 0$$

$$= -\ln(m_j) - 1 - \alpha - \beta E_j = 0 \Rightarrow \ln(m_j) = \underbrace{-1 - \alpha - \beta E_j}_{-\alpha'}$$

$$\ln(m_j) = -\alpha' - \beta E_j$$

$$m_j^* = e^{-\alpha'} e^{-\beta E_j}$$

* E_j negativo, a mayor E_j , menor m_j^*
 Los sistemas tienden a estar en menor nivel energético

$$\sum_j m_j^* = M = \sum_j e^{-\alpha'} e^{-\beta E_j} = e^{-\alpha'} \sum_j e^{-\beta E_j}$$

$$e^{-\alpha'} = \frac{M}{\sum_j e^{-\beta E_j}} \rightarrow \text{Plug in previous expression}$$

$$m_j^* = \frac{M}{\sum_j e^{-\beta E_j}} e^{-\beta E_j} \rightarrow \frac{m_j^*}{M} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = P_j$$

Very important
 Very important
 Very important

Be aware that $\sum P_j = 1$

To find β we realize that must be a function of T

~~β~~ $\beta = \beta(T)$ and must have units of $1/\text{energy}$

Value of β and value of Properties

For a general property L , we can write

$$\bar{L} = \sum L_j P_j \rightarrow \text{We apply this to energy}$$

$$\bar{E} = \bar{E}(N, V, \beta) = \frac{\sum_j E_j e^{-\beta E_j(N, V)}}{\sum_j e^{-\beta E_j(N, V)}}$$

Apply to pressure

$L_j = P_j$ = Value of pressure in Energy level 'j'

$$P_j = -\left(\frac{\partial E_j}{\partial V}\right)_N$$

$$dE = dU = TdS - PdV \rightarrow -P = \left(\frac{\partial E}{\partial V}\right)_N$$

Average Pressure

$$\bar{P} = \frac{\sum -\left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}}{\sum e^{-\beta E_j}} \quad (2)$$

Evaluation of β

Average Energy = $\bar{E} = \bar{E}(N, V, \Delta) = \frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}} = \frac{f(x)}{g(x)} \quad (1)$

$\left(\frac{\partial \bar{E}}{\partial V}\right)_{N, \beta} = \frac{f'g - g'f}{g^2}$

$g' = \sum -\beta e^{-\beta E_j} \cdot \left(\frac{\partial E_j}{\partial V}\right) \quad (4)$

$f' = \sum \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j} + \sum E_j (-\beta) \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j} \quad (3)$

$\left(\frac{\partial \bar{E}}{\partial V}\right)_{N, \beta} = \frac{\sum E_j e^{-\beta E_j} \left(\sum \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j} + \sum E_j (-\beta) \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}\right) - \sum -\beta \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j} \sum E_j e^{-\beta E_j}}{\left(\sum e^{-\beta E_j}\right)^2}$

$\left(\frac{\partial \bar{E}}{\partial V}\right) = \frac{\sum \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}}{\sum e^{-\beta E_j}} - \frac{\beta \sum \left(\frac{\partial E_j}{\partial V}\right) E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}} + \frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}} \left[\frac{\beta \sum \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}}{\sum e^{-\beta E_j}} \right]$

This is average pressure

$L = \frac{\sum L_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}$

Average Energy

β times average pressure

Here L_j is

$E_j \left(\frac{\partial E_j}{\partial V}\right)$

$\overline{PE} \neq \bar{P} \bar{E}$

$\left(\frac{\partial \bar{E}}{\partial V}\right) = -\bar{P} + \beta \overline{PE} - \beta \bar{P} \bar{E} \quad (5)$

Differentiate \bar{P} with respect to β

$\left(\frac{\partial \bar{P}}{\partial \beta}\right) = \bar{E} \bar{P} - \overline{PE} \quad (6)$

$\left(\frac{\partial \bar{E}}{\partial V}\right) = -\bar{P} - \beta \left(\frac{\partial \bar{P}}{\partial \beta}\right)$

$\left(\frac{\partial \bar{E}}{\partial V}\right) + \beta \left(\frac{\partial \bar{P}}{\partial \beta}\right) = -\bar{P} \quad (7)$

HOMEWORK: SHOW THAT

10/31/22

$$\left(\frac{\partial U}{\partial V}\right)_T - T \left(\frac{\partial P}{\partial T}\right)_V = -P \quad (8) \quad \left(\frac{\partial E}{\partial V}\right)_T - T \left(\frac{\partial P}{\partial T}\right)_V = -P$$

Postulate: $\beta = 1/T$

$$d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT \rightarrow dT = -T^2 d\left(\frac{1}{T}\right)$$

What if $\beta = \frac{1}{T}$

$$\beta = \frac{\text{Constant Unit}}{T} = \frac{1}{k_B T}$$

11/02/22

Canonical Ensemble Partition Function

$$Q(N, V, T) = \sum e^{-E_j/k_B T}$$

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

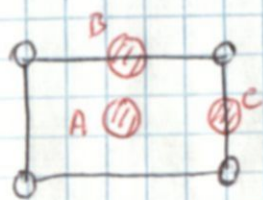
$$P_j = \frac{e^{-E_j/k_B T}}{\sum e^{-E_j/k_B T}} = \frac{e^{-E_j/k_B T}}{Q(N, V, T)}$$

$$dA = -S dT - P dV + \mu dN$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V, N} = -\frac{\partial}{\partial T} (-k_B T \ln(Q))$$

$$S = k_B \ln(Q) + k_B T \left(\frac{\partial \ln(Q)}{\partial T}\right)_{V, N}$$

* Cute example: Adsorption surface Three energy levels



E_C → Highest, less probable $\Omega = 2$
 E_B → $\Omega = 2$
 E_A → Lowest, most probable $\Omega = 1$

$$Q(N, V, T) = \sum_j e^{E_j/k_B T} = \sum_E \Omega(N, V, E) e^{-E/k_B T}$$

GRAND CANONICAL ENSEMBLE (μ, V, T)

9 Boxes within thermal bath (constant T) and same volume (constant V) the molecules can go from one box to another but no out of the system (constant μ)



* Un grand canonical ensemble se compose de multiples ensembles canoniques. Cada caja que tiene el mismo número de partículas forman un ensemble canonico

$$\sum_N \sum_j m_{N_j} = M = \text{Total number of systems}$$

$$\sum_N \sum_j m_{N_j} E_j = E = \text{Total energy of the ensemble}$$

$$\sum_N \sum_j m_{N_j} N = N = \text{Total number of atoms}$$

$$W(M, N_j) = \frac{M!}{\prod_N \prod_j m_{N_j}!} \quad P_{N_j} = \frac{m_{N_j}^*}{M}$$

Taking the derivative

$$P_{N_j} = \frac{e^{-\beta E_{N_j}} e^{\mu N_j / kT}}{\sum_N \sum_j e^{-\beta E_{N_j}} e^{\mu N_j / kT}} \quad E = \sum_N \sum_j e^{-\beta E_{N_j}} e^{\mu N_j / kT} = \sum_N Q(N, V, T) e^{\mu N / kT}$$

$$PV = k_B T \ln(\Xi(N, P, T))$$

* Este sistema funciona para problemas de equilibrios de fase

ISOTHERMAL, ISOBARIC ENSEMBLE (N, P, T)

$$\Delta(N, P, T) = \sum_E \sum_V \Omega(N, V, E) e^{-E/kT} e^{-PV/kT}$$

$$G = -k_B T \ln(\Delta(N, P, T))$$

MICROCANONICAL ENSEMBLE (N, V, E)

Partition function = $\Omega(N, V, E)$ = degeneracy

* It's the number of atomic arrangements that have the level E

$$S = k_B \ln(\Omega(N, V, E))$$

For Canonical (retaking)

$$A = -k_B T \ln(Q) \rightarrow dA = -PdV - SdT + \mu dV$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{TN} = k_B T \frac{\partial \ln Q}{\partial V}$$

For Grand Canonical

$$pV = kT \ln \Omega(N, V, T) \rightarrow d(pV) = SdT + Nd\mu + PdV$$

For Isothermal, isobaric

$$\bar{G} = -k \ln \Delta(N, P, T) \quad d\bar{G} = -SdT + VdP + \mu dN$$

$$S = \left(\frac{\partial \bar{G}}{\partial T} \right)_{N, P} = -k \ln \Delta + kT \left(\frac{\partial \ln \Delta}{\partial T} \right)_{P, N}$$

$$V = \left(\frac{\partial \bar{G}}{\partial P} \right)_{N, T} = -kT \left(\frac{\partial \ln \Delta}{\partial P} \right)_{N, T} \quad \mu = \left(\frac{\partial \bar{G}}{\partial N} \right)_{T, P} = -kT \left(\frac{\partial \ln \Delta}{\partial N} \right)_{T, P}$$

Micro canonical

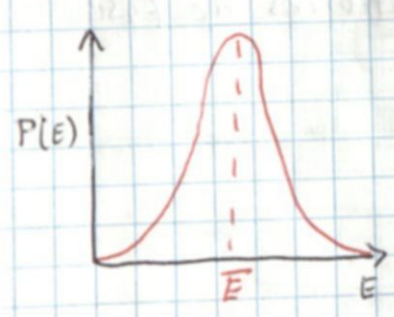
$$S = k \ln \Omega(N, V, E) \rightarrow dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

FLUCTUATIONS AND AVERAGES

$$\langle L \rangle = \bar{L} = \sum_j L_j P_j$$

Postulate: \bar{L} = Value of L measured in laboratory

Canonical ensemble and value of \bar{E} (N, V, T)



$$\sigma_E^2 = \overline{(E - \bar{E})^2} = \bar{E}^2 - (\bar{E})^2$$

$$= \sum_j E_j^2 P_j - (\bar{E})^2 \quad (1)$$

Some algebra on (1)

Recall

$$\sum E_j^2 P_j = \frac{1}{Q} \sum E_j^2 e^{-\beta E_j} \quad Q = \sum e^{-\beta E_j / kT} \quad \beta = 1/kT$$

Aside we work on $\frac{\partial}{\partial \beta} (e^{-\beta E_j}) = -E_j e^{-\beta E_j}$

$$\frac{\partial}{\partial \beta} (E_j e^{-\beta E_j}) = -E_j^2 e^{-\beta E_j}$$

$$\sum E_j^2 P_j = -\frac{1}{Q} \frac{\partial}{\partial \beta} \left(\sum E_j e^{-\beta E_j} \right) = -\frac{1}{Q} \frac{\partial}{\partial \beta} \left[\sum Q \left(\frac{E_j e^{-\beta E_j}}{Q} \right) \right]$$

$$= -\frac{1}{Q} \frac{\partial}{\partial \beta} (Q \bar{E}) = -\frac{\partial \bar{E}}{\partial \beta} - \frac{\bar{E}}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E} \frac{\partial \ln Q}{\partial \beta} \quad (2)$$

We operate on the first term of the right hand side

Be change from β to $1/kT$

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \bar{E}}{\partial T} \frac{\partial T}{\partial \beta} = \frac{\partial \bar{E}}{\partial T} \frac{\partial}{\partial \beta} \left(\frac{kT}{k} \right) = \frac{\partial \bar{E}}{\partial T} \frac{\partial}{\partial \beta} \left(\frac{1}{k\beta} \right) = \frac{\partial \bar{E}}{\partial T} \left(\frac{-1}{k\beta^2} \right) = \frac{\partial \bar{E}}{\partial T} \left(\frac{-kT^2}{k} \right)$$

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \bar{E}}{\partial T} (-kT^2) = -kT^2 \frac{\partial \bar{E}}{\partial T} \quad (3)$$

The last term to change so it's depending on temperature

$$\bar{E} \frac{\partial \ln Q}{\partial \beta} = \bar{E} \frac{\partial \ln Q}{\partial T} \frac{\partial T}{\partial \beta} = \bar{E} \left[-kT^2 \left(\frac{\partial \bar{E}}{\partial T} \right) \left(\frac{\partial \ln Q}{\partial T} \right) \right]$$

In Canonical this is \bar{E}^2

$$\text{So } \bar{E} \frac{\partial \ln Q}{\partial \beta} = -\bar{E}^2 = -\bar{E}^2 \quad (4)$$

We can now re-write eq. (1) and eq. (2)

$$\sigma_E^2 = -\frac{\partial \bar{E}}{\partial \beta} - (-\bar{E}^2) - \bar{E}^2 = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \left(\frac{\partial \bar{E}}{\partial T} \right) \quad \text{* Remember, that } U \approx \bar{E} \text{ here}$$

$$\sigma_E^2 = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V$$

* La apertura del error depende del sistema, y realmente lo que nos da resultados es

$$\frac{\sigma_E}{\bar{E}} = \frac{(kT^2 C_V)^{1/2}}{\bar{E}} \quad \text{* Porque así lo compara contra el sistema en } \gg 1$$

Relative magnitude of uncertainty compared to the mean

Consider Ideal Gas

$$\frac{\sigma_E}{\bar{E}} = \frac{(kT^2 C_V)^{1/2}}{\bar{E}} \approx \frac{(kT^2 Nk)^{1/2}}{NkT} = \frac{kT N^{1/2}}{NkT} = \frac{1}{\sqrt{N}}$$

$$\frac{\sigma_E}{\bar{E}} = \frac{1}{\sqrt{N}}$$

$$\text{* } C_V = \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left. \frac{\partial (Nk)}{\partial T} \right|_V$$

N	σ_E / \bar{E}
100	0.1
10,000	0.01
1×10^6	0.001
1×10^{24}	1×10^{-12}

→ Macroscopic analysis

FOR GRAND CANONICAL

Constant μ, V, T
Fluctuant N, P, E

$$\sigma_N^2 = \sum N^2 P_i - \bar{N}^2 \longrightarrow \sigma_N^2 = \frac{\bar{N}^2 kT}{V} \beta$$

Final solution η

$\beta \rightarrow$ Isothermal Compressibility

And so

$$\frac{\sigma_N}{\bar{N}} = \left(\frac{kT}{V} \beta \right)^{1/2}$$

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \mu}$$

Homework: Show $\frac{\sigma_E}{\bar{E}} \approx \frac{1}{\sqrt{N}}$ for ideal gas ($PV = NkT$)

SIMPLIFICATION OF PARTITION FUNCTION

Consider system of distinguishable particles where total energy can be written as a sum of energies of individual particles.

Particles denoted by: a, b, c, \dots } E^a Particle a
Their energy states by: i, j, k } E_i Energy state i

$$Q(N, V, T) = \sum_m e^{-E_m / kT} = \sum_{i, j, k} \exp [E_i^a + E_j^b + E_k^c + \dots] / kT$$

$$= \underbrace{\sum_i e^{-E_i^a / kT}}_{q_a} \underbrace{\sum_j e^{-E_j^b / kT}}_{q_b} \underbrace{\sum_k e^{-E_k^c / kT}}_{q_c} \sum \dots$$

$$Q(N, V, T) = q_a q_b q_c \dots$$

If the particles are the same but distinguishable

$$q_a = q_b = q_c = \dots$$

11/07/22

$$Q = q^N$$

Now, if the particles are the same but indistinguishable

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

24 oct

Statistical Mechanics,

Quantum Mechanics $\Psi(\underline{q}, t)$

coordinates \swarrow
time \nwarrow

system of particles

$\Psi(\underline{q}, t)$: probability that at time t , system
occurs between q_1 and $q_1 + dq_1$
 q_2 and $q_2 + dq_2$

~~Do not write this part~~

$$\text{Probability} = \Psi^*(\underline{q}, t) \Psi(\underline{q}, t) dq_1 dq_2 d\mathbf{q}$$

$$\int \Psi^*(\underline{q}, t) \Psi(\underline{q}, t) dq_1 dq_2 = 1$$

We are interested in $\Psi(\underline{q})$

Schrodinger

$$H\Psi = E\Psi$$

Equation

H = Hamiltonian operator

$$H = \frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r})$$

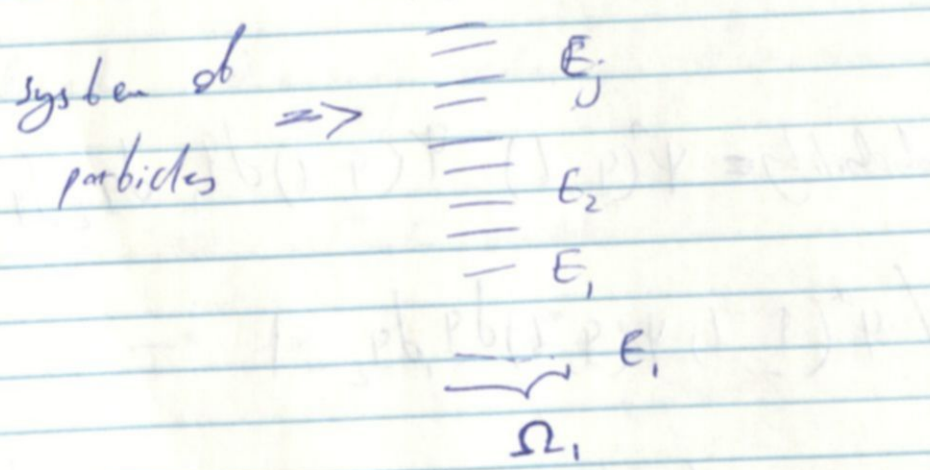
kinetic energy potential energy

$$A x = \lambda x$$

⇒ Many ψ^s and E values satisfy above eqⁿ

$$\text{eg } H \psi_j = E_j \psi_j$$

energy states of the system



energy → $\sum e^{-\beta E_j}$
partition function

system of
particles

\Rightarrow Distinct energy states ϵ_j
with degeneracies Ω_j

Energy \uparrow

Math preliminary

Variable assumes discrete values

u_1, u_2, \dots, u_N with probabilities
discrete random variable

$p(u_1), p(u_2), \dots, p(u_N)$

Average value of u $= \bar{u} = \frac{\sum u_i p(u_i)}{\sum p(u_i)} = \sum_{i=1}^N u_i p(u_i)$

The mean of a function of u

$$\overline{f(u)} = \sum_i f(u_i) p(u_i)$$

\leftarrow this we know

If u is a continuous variable

and $p(u) du$ = probability that system (next page)

is between u and $u + du$

$$\vec{F}(u) = \int_u^{\infty} f(u) p(u) du$$

Distribution of objects in states

N distinguishable objects

$$\left(\begin{array}{l} \text{number of ways} \\ \text{of arranging them} \end{array} \right) = N(N-1)(N-2) \dots \cdot 1$$

~~the~~ Number of ways of arranging N objects

such that N_1 are in state 1,

N_2 are in state 2, -

$$= \frac{N!}{N_1! \times N_2!}$$

stirling approximation

$$N! \approx (1)(2)(3) \dots (N)$$

$$\ln N! \approx \sum_j \ln j$$

$$\ln N! \sim N \ln N - N$$

~~very large~~

$N \rightarrow \infty$
very large

Lagrange's undetermined Multiplier method

Find the maximum of function $f(x_i)$: $f\{x_i\}$

subject to constraint: $g\{x_i\} = 0$

\Rightarrow same as finding maximum of:

$$f\{x_i\} - \lambda g\{x_i\}$$

$$\Rightarrow \left(\frac{df}{dx_i} \right) - \lambda \left(\frac{dg}{dx_i} \right) = 0$$

$$g\{x_i\} = 0$$

Find maximum of products of mole fractions for

a binary system $f(x_1, x_2) = x_1 x_2$

Constraint $x_1 + x_2 = 1$

$$g(x_1, x_2) = x_1 + x_2 - 1 = 0$$

$$\frac{\partial f}{\partial x_1} = x_2 \quad \frac{\partial g}{\partial x_1} = 1$$

$$\frac{\partial f}{\partial x_2} = x_1 \quad \frac{\partial g}{\partial x_2} = 1$$

$$1) \quad \frac{\partial f}{\partial x_1} - \lambda \frac{\partial g}{\partial x_1} = 0 \Rightarrow x_2 - \lambda = 0 \Rightarrow x_2 = \lambda$$

$$2) \quad \frac{\partial f}{\partial x_2} - \lambda \frac{\partial g}{\partial x_2} = 0 \Rightarrow x_1 - \lambda = 0 \Rightarrow x_1 = \lambda$$

$$\textcircled{1}, \textcircled{2} \Rightarrow x_1 = x_2 = \lambda$$

$$x_1 + x_2 = 1 \Rightarrow 2\lambda = 1 \Rightarrow \lambda = \frac{1}{2}$$

So maximum value of $f(x_1, x_2) = 0.25 = x_1 x_2$

Ensemble

objective: calculate Macroscopic (thermodynamic)

properties in terms of molecular properties.

problem: large number of molecules

statistics

not Arithmetic average but statistical ^{mechanical} average

→ Ensemble average value of property

postulate. Average value of property

calculated as an ensemble average can be

equated to the thermodynamic property value.

November 9th

Quantum \rightarrow classical

N particle system

$$Q = \frac{q^N}{N!} \rightarrow q = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} V$$

\uparrow $\frac{V}{\Lambda^3}$

$$\Lambda = \left(\frac{h^2}{2\pi m kT} \right)^{1/2}$$

Hamiltonian: $H(p, q) = K(p) + U(q)$

momenta \quad coordinates \quad potential energy

kinetic energy \nearrow

$P = mv$

$$K.E. = \frac{1}{2} m v^2 = \frac{1}{2} \frac{p^2}{m}$$

one particle

$$Q = \sum_j e^{-\beta E_j}$$

$$E \leftrightarrow H(p, q)$$

instead of this

— ✓ is this
— →
—
—

large number of atoms \Rightarrow very large number of energy levels that are closely spaced.

$$A(P, q) = k_B U$$

this is function of temperature

Chapter 7

$$Q_{\text{classical}} = \int \dots \int e^{-\beta H(P, q)} dP dq$$

dP_1, dP_2, \dots, dP_N dq_1, dq_2, \dots, dq_N

1 particle:

$$Q_{\text{classical}} = \int \dots \int \exp\left[-\beta \left(\frac{P_x^2 + P_y^2 + P_z^2}{m}\right)\right] dP_x dP_y dP_z dx dy dz$$

$$Q_{\text{classical}} = (2\pi m kT)^{3/2} V$$

$$\int dx dy dz = V$$

N-particle system

classical

$$Q_{\text{classical}} = \frac{1}{N! h^{3N}} \int e^{-\beta H(\mathbf{p}, \mathbf{q})} d\mathbf{p} d\mathbf{q}$$

$$= \frac{1}{N! h^{3N}} \int e^{-\beta \left[\frac{1}{2m} \sum_i \mathbf{p}_i^2 + U(x_1, y_1, z_1, \dots, x_N, y_N, z_N) \right]} d\mathbf{p} d\mathbf{q}$$

$$Q_{\text{classical}} = \frac{1}{N!} \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3N}{2}} Z_N$$

we should know this

Potential energy part

$$Z_N = \int e^{-\beta U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)} dx dy dz$$

= classical configuration integral

Configurational partition function

particle positions: Radial Distribution Function (RDF)

probability of observing a configuration

$$\underline{r}^N = \{r_1, r_2, \dots, r_N\} \propto P(\underline{r}^N) = \frac{e^{-\beta U(\underline{r}^N)}}{\int e^{-\beta U(\underline{r}^N)} d\underline{r}^N}$$

probability distribution for finding particle 1

at r_1 and particle 2 at r_2 in an

N particle system $\int P(\underline{r}^N) \Big|_{r_1, r_2} d\underline{r}_3 d\underline{r}_4 d\underline{r}_5 \dots d\underline{r}_N$

$$\rightarrow P^{2/N}(r_1, r_2)$$

particle 1 at r_1 and particle 2 at r_2

$\sim \sim \sim \sim$ any particle at r_1 and

any particle at $r_2 \sim \sim \dots$



$$P^{2/N}(r_1, r_2) = N(N-1) P^{2/N}(r_1, r_2)$$

any 2 particles at r_1 and r_2

Consider ideal gas:

$$P_{IG}^{(2/N)}(T_1, T_2) = P^{(1/N)}(T_1) P^{(1/N)}(T_2)$$

$$= \left(\frac{1}{V}\right) \left(\frac{1}{V}\right)$$

$$\int_{IG}^{2/N} (T_1, T_2) = N(N-1) \left(\frac{1}{V}\right) \left(\frac{1}{V}\right)$$

Question of 1 student

$$Q(N, V, T) = \sum_j e^{-E_j/kT} = \sum_{\epsilon} \Omega(N, V, \epsilon) e^{-\epsilon/kT}$$

~~10~~ -
-
-
-