Madarju.com

Thermodynamics 2

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(eq) لا يوجب :: شرط واحد يتم في قمة

* شروط equilibrium :- شرط واحد يتم في قمة

- Thermal equilibrium: The Temp equal at every part of the syst
- Mechanical eq → ضغط متساوي
  Pressure equal at every part of the system

$P_{room} = \left(\frac{3 \times 1 \times 1.0}{2 \ \rho \ g}\right) Pa = 30 \ Pa$, 0.9 bar = 90000 Pa = ضغط جوي العادة

(*) لو بنا نقول = لا يوجب eq (لا يوجد مثالية) للواقع لا يوجد فرق كبير

شرط صعب - chemical or material equilibrium :

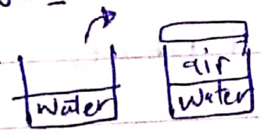
heat, work, mass → sys ← طرق تغير الحالة

Gibes energy for pure component, or, fugacity for mixture for each component for each phase equal

fugacity

* how much the component in specific Phase (ولا مرتاحة) (مش مرتاحة) in that phase !!

* مثال: حطينا (ماء + هواء) في كاسة فتحناها للهواء، ماذا سيحدث



هواء الـ fugacity مع ماء = مضغوط فيتبخر

الـ air يقلل Fugacity

فتقليل الـ component تبعي مرتاحة، لا مش مرتاحة في phase معين

If there is a chemical eq., fugacity for each component must be equal for each phase
What does that mean?

انواع الـ eq :

① Phase eq (more than Phase) → physical eq.

② Chemical eq → Rxn

cancellation Rxn → اختصار CO_2 الى ذرة

Calcium Carbonate

$CaCO_3 \rightarrow CaO + CO_2$ (Roter drier)

↓

تطبيقات

↓

الانشائي

أكسيد + ماء ← هيدروكسيد

$CaO + H_2O \rightarrow Ca(OH)_2$ هيدروكسيد كالسيوم (أكسيد كالسيوم)

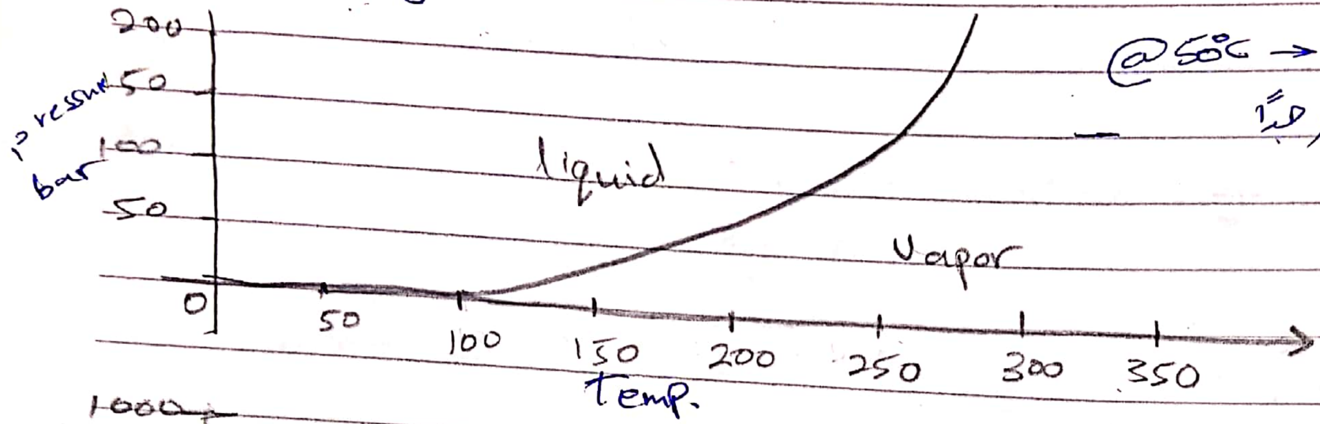
$CO_2 + H_2O \rightarrow H_2CO_3$ طعم الحمض في البيرة ← كربونيك

No:------------ Date: 11th feb 2020

MM SCFD (standard cubic feet per day) 1000,000 decatherm → وحدة انرجي بريطانية

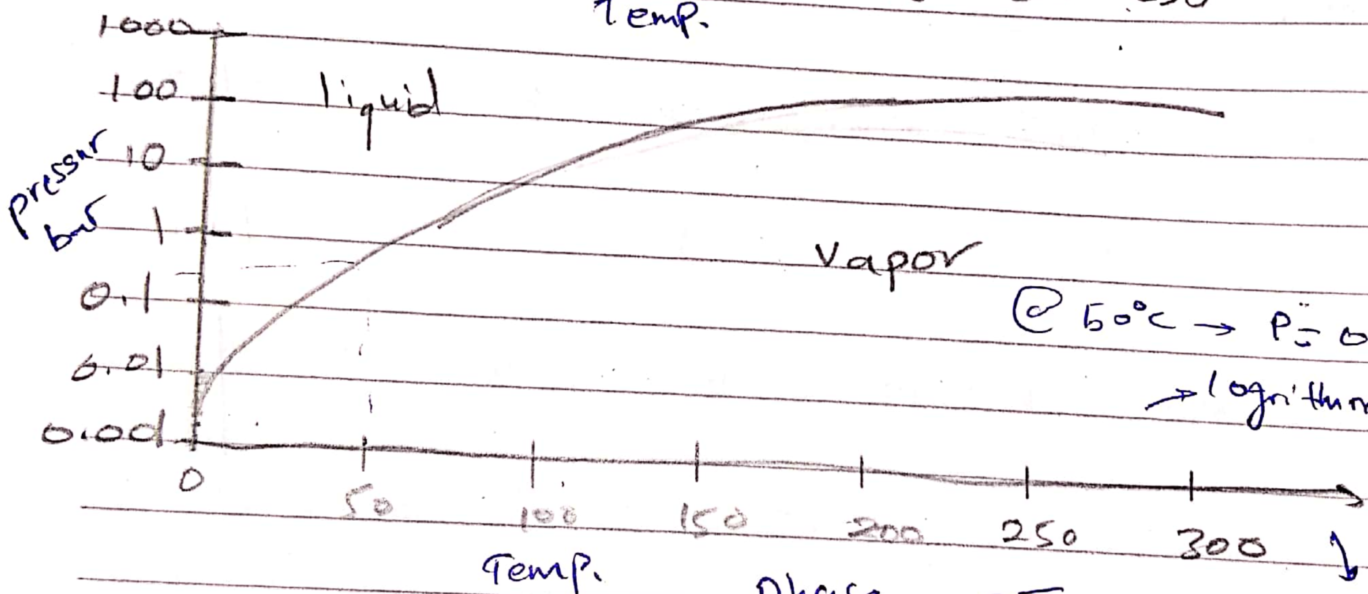
M SCFD 1000

Phase diagram



@50°c → P = ?

صغير جداً



@50°c → P = 0.2 bar

→ logrithmic

Phase diagram PT جزء من

* كل unit في logrithmic scale = هي عشر أضعاف الي قبلها

* Rang wide → we use log-log scale

* نقرأ القيم على log-log :

cicles = القيمة وعشر أضعافها، هكذا بدون حتى لو حطولنا نقطاً

الي بينهم digits

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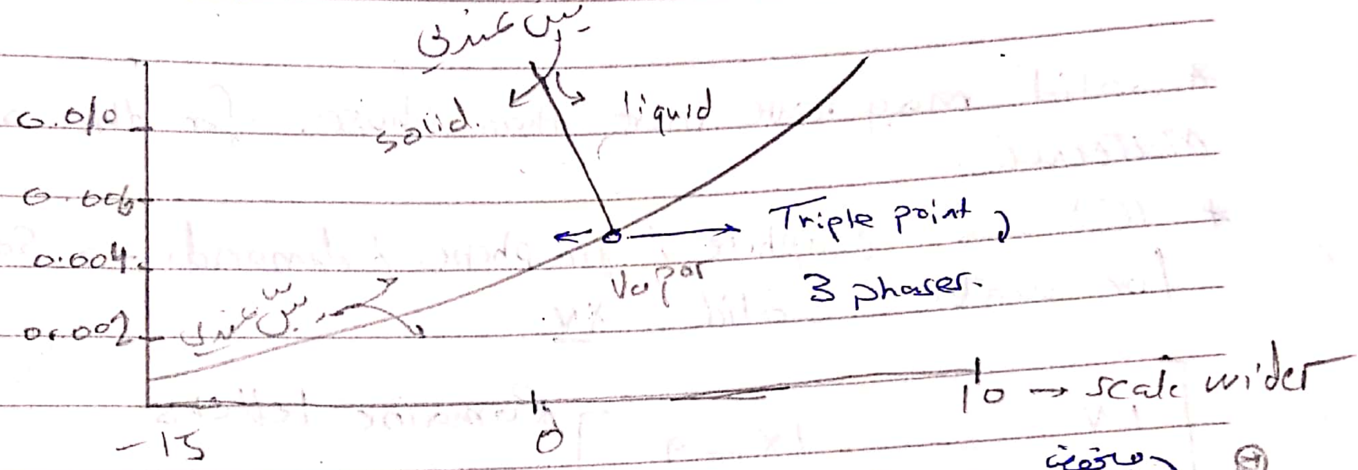
in log-scale → تقسيم ال scale الى قدام ثلث الثلاث

↑ ثلث ③ ثلث ② → 5 ; ثلث ① → 2 ; 0.01, 0.005, 0.002, 0.001 → Interpolation easier

log → الاشي → take it as interpolation don't take it as a linear.



Solid → vapor = sublimation تسامي ⊖ ماص حرارة عالي

Vapor → solid = deposition ترسيب ⊕ طاقة ساري لا يحرك → منخفض

⊛ Vapor - liquid - solid (موجودين) @ Triple Point

Vapor at low Pressure or Temp low.

@ lower Temp doesn't mean there are just liquid and solid

* Temp↓ & P↓ → There is vapor phase

cloud ; what is phase?

liquid + vapor

لو نزلت الغيمة من طبقة جو منخفض؟

→ يصير vapor و بتروح الغيمة.

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liquid or solid ← (مخلوط) ← ثلاجة ↓ درجة حرارتها
وكله يطلع من الثلاجة
لـ liquid ← (بخار) ← وليش؟ ← يتبخر من الشرفة
مخففة بالسرعة زي ما مثلا الزيت

* solid may have more than phase for the same Material

* (C) → graphite / graphene / dimond. → Solid
for water solid XV

IV	IX → 9	Romaine letters
V → 5	X → 10	Millennium: ألفية
VI → 6	XI → 11	أكبر حرف للعد بالرومانية
VII → 7	XII → 12	
VIII → 8	XIII → 13	

ملیون = (ألف ألف)

* solid phases → أكثر من شكل
↘ difference between different solid phase ⇒ structure

* snow of wether ⇒ more liquid content
ثلج → in Ref. → more solidity → pressure of liq.
يعني (liquid) فوق بعضه

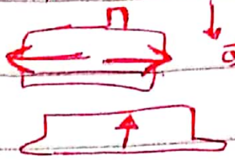
* graphite — diamond] structure
↓ Sheets (sp) — ↓ Pyramids
→ shear // surface

No: .... Date: ....

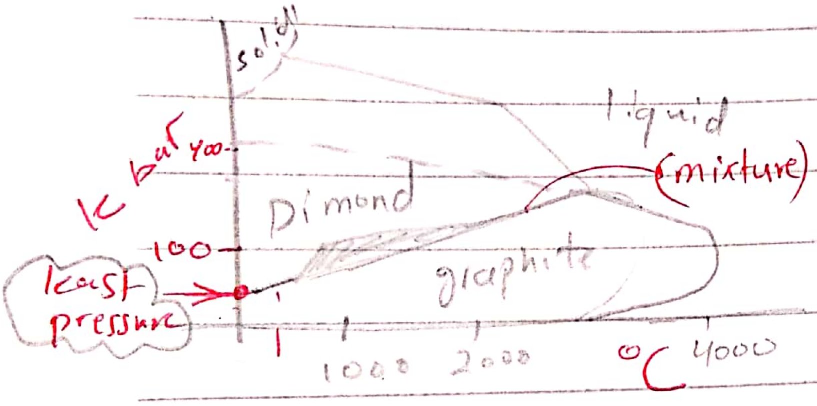
graphite application? + Battery

shear تحمل
heat ↓ توزيع,

* Car breaks
+ clothes iron ↓ توزيع الحرارة



+ heat exchanger → مكلف جدا
↓
inert for corrosion materials.
Hf | H_2SO_4 قوي



→ (least Pressure) to make dimond from graphite?
20 Kbar

* قراط ≡ $\frac{1}{5}$ gram → dimond

No: App. of buckyballs Date: 16th – feb – 2020

* Gibbs energy أقل ← في الظروف الاعتيادية ← graphite

⇒ على المدى البعيد تتحول dimond ← graphite

ليش ما تتحول قدام عيوننا؟ لأنه kinetic (قليل) ← بطيء Rate of conversion

قليل

+ مسألة kinetic مش equilibrum.

* الشكل الجديد للكربون:

Bucky balls → buckminsterfullerene → C_{60} ([illegible])

Single-walled CNT → Carbon nano tube

multiwalled CNT

graphene

* what is the significant about that materials?

→ Cruel material, very cruel material

for example: (CNT) → fibers shape → Stronger by six times than iron.

→ Very high thermal conductivity.
most common: copper

→ very high electric conductivity
The loss in our electrisity in our common copper wires about 5 % in the whole world

* Why not to use?
Because these materials on development (R&D), not exist as a product ready to use

→ Using as an alternative to Silicone material
The first computer → ≈1940 it used light bulb instead of resistors. → 1 megahertz

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→ Catalists in Rxn,
we use material of non-affected surface of catalists.
* example of used catalists:
Platen, gold, Pd →
not to enter rxn, but may be deactivated

→ molecular gear → and many part of things to be in molecular level
(bottom-up) → no wast of materials
↳ no need to repair parts because it already had the repairing molecules

→ Minimizing the manufacturing space.

* Even though these applications have militarily ethical and political problem:
↓ using so preci weaponry
[أخلاقية، سياسية]
↓ ex: artifical flies.
Biostasis

top-down → as usuall with nano technology it will become (down-top.)

* elevator to moon!!!

* 11 km/sec

Gibbs Energy 18th - feb - 2020.

Reviews Equilibrum: → ① Thermal Eq. → Temp.
② Mechanical eq → P.
③ Chemical → fugacity But as a Pure component → Gibbs energy

Chemical Eq:

⇒ Gibbs energy:

⇒ From steam table:

@ 100°C for sat water → two phase

Gibbs energy for steam = Gibbs energy for liquid.

⇒ Prove that:

$G = H - TS$ (T in Kelvin)

⊛ @ 100°C in water steam table:

$h_g = 2676.1$ $s_g = 7.3549$ kJ/kg·k $T = 373K$

$h_L = 419.04$ $s_L = 1.3069$ kJ/kg·k

$G^g = 2676.1 - 373 * 7.3549 = -67.277 \frac{kJ}{kg}$

$G^L = 419.04 - 373 * 1.3069 = -68.4337 \frac{kJ}{kg}$

$\Delta G = -68.4337 - -67.277 \simeq 1.16$ (accepted)

→ $G^g \simeq G^L$ Proved ✓

And that Principle Valid for (R-134) table.

⇒ constrains for eq: $T_{vapor} = T_{liquid} = 100°C$ → Thermal.

$P_{vapor} = P_{liquid}$ → Mechanical

$G_V = G_L$ → what is moved

∴ The system is (eq)

No:---------- Date:--18th--feb-2020

but superheated steam table, is eq applied?

No, $G_V < G_L$

Gibbs energy when subcooled exist:

$G_L < G_V$

→ كيف اطلع Gibbs energy حتى على الخواص موجودة فيه Two phases

phase @ Temp. higher than 100°C → superheated steam

↑

100°C @ the same pressure

↓

phase @ Temp. lower than 100°C → subcooled liquid.

estimate [Gibbs energy]

- 110 °C
- 120 °C
- 140 °C
- ⋮

] at the same P

⊛ plot @ the same P for Gibbs energy ←

estimate Gibbs energy

- 90°C
- 80°C
- ⋮

⊛ plot @ The same(P) @ The same graph ←

intersect: equilibrium

extrapolation for liquid → @ high Temp. Gibbs energy for liquid > Gibbs energy for vapor

extrapolation for vapor → phase stable = liquid

⊛ Gibbs energy continuous fxn:

no Discontinuity

→ spesific volume → fxn Discont.

→ specific enthalpy → " "

→ specific internal energy → fxn Discont.

→ S → fxn "

⇒ from discountinous fxn ∄ you can fon Cont fxn

Gibbs fxn

No: ..... Date: 18th feb

⇒ (C_p) (C_v) ∴

$\left(\frac{\partial H}{\partial T}\right)_P$

its Derivative discont. ∴ Discont fxn.

Cp for vapor ≠ cp for liquid

* liquid → vapour
vapor → liquid
solid → liquid
→ [first order first transition]

The single cont. fxn = Gibbs energy fxn.

* Second order First transition

In solids → how dimond transites to graphit and vice versa → There is a continuty fxn.

* → Table : (ice water – vapor) phase :

@ -12 °C : → يمين → (safe side)

$g^v = h^v - T s^v = 2478.4 - (261.15)(9.549) = -1532 \frac{kJ}{kg}$

$g^s = h^s - T s^s = -358.17 - (261.15)(-1.3130) = -15.28 \frac{kJ}{kg}$

minus! because of reference point: That The ref. point = 0.01 Triple point

NOTE :-

g phase ① = g phase ② → Pure Component

* multi component system → fugacity

(-15.32 - -15.28) ≠ 0 (Not exactly 0! Why?

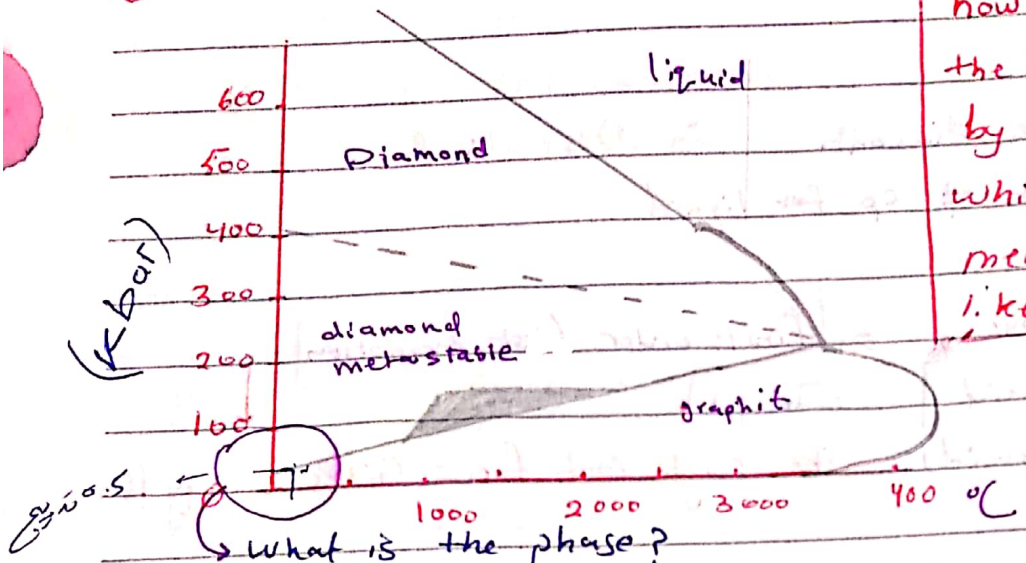
* Steam tables have percentage of error in comparison with experimental data ; so range of accepted error $\pm 1 \frac{kJ}{kg}$

16.32 ~ -15.32 ~ -14.32

اي نقطة ضمن المدى مقبولة لا تقل عن -15.32

No:---------- Date:---15th---feb-2020

⊛ Phase diagram of carbon



Idea!
how to express the transition curve by quantities, which can be measured experimentally like P, V, h ... e.c

→ what is the phase?
graphite or diamond or mixture
↳ saturation curve → 2 phase

So; $g^{graphite} = g^{diamond} \rightarrow h^g - Ts^g = h^d - Ts^d$

$(h^g - h^d) = T(s^g - s^d)$

Δh ← transition

we can estimate experimentaly by DSC;

* we face a problem; because we can't estimate experimentally!

(entropy) في الطبيعة و (gibbs Energy) لا يمكن

$$\Delta g = -P\Delta V$$

g fxn of T and P

$$dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$$

from maxwell relations

two variable → moles change

$$dg = v\,dp - s\,dT \quad (?)$$

$$\left(\frac{\partial g}{\partial p}\right)_T = v \quad ; \quad \left(\frac{\partial g}{\partial T}\right)_p = -s$$

$$\left(\frac{\partial f}{\partial x}\right)_T = 0$$

[Clausius Clapeyron] العلاقة بين الضغط والحرارة

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow \text{vapor pressure} \nearrow P$$

* Qualitative Q: at which circumstances can we converte the graphite to diamond?

from phase diagram; at normal Temp. and at about 20,000 bar. but if there is no phase diagram

⇒ specific volume for graphite, specific volume for diamond ⇒ ρ

⇒ Δh ✓ (diamond and graphite)

→ experimental or → calculated from previous equations

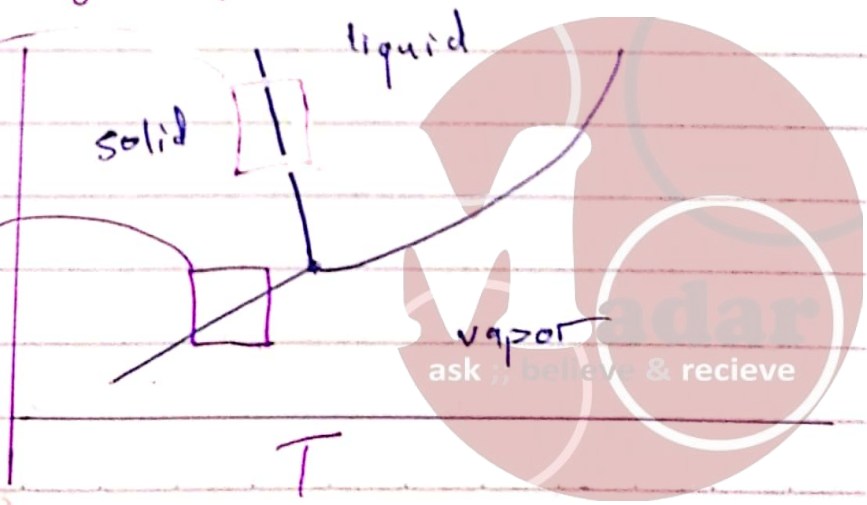
* Back to phase diagram of water:

→ life application: ρ

Ice skating boots

⊛ ΔV (solid, vapor)

Δh



No:---------- Date:----------

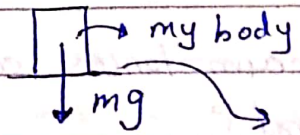
$h_v > h_L$ $\hat{V}_L$ so ΔV (-)

$S_s < S_L$ → Just for water

* Sky skating → knife Looklike ?? Why ??

↑ pressure = $\frac{\text{Fore}}{\text{Area}\downarrow}$ so; under high $\underline{P}$, the

ice under ice skeating boot's knife turns to liquid so the friction becomes Less → It's look like water skeating



$P = \frac{mg}{Area}$ → Area of normal boot > Area of knife

↑P (ice of water) turn to liquid, whereas other material ↑P ice of other material → they become more ice) and ↑P ↑S

⊕ space equipment → space boot has big area.
↑P → the movement will be harder

No: Classius Clapeyron Date: 23th - feb - 2020

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} \quad \text{---- } ⊛⊛$$

$du = T\,ds - P\,dV$ ⊛ → Energy balance for closed system

$d(PV) = P\,dV + V\,dP$

$d(TS) = T\,ds + S\,dT$

$g = (u + pv) - TS$

$dg = d((u+P.v) - TS) = \boxed{du} + P\,dv + V\,dp - T\,ds - s\,dT = dg$

↓ substitute with ⊛

$T\,ds - P\,dv + P\,dv + V\,dp - T\,ds - s\,dT = dg$

$\therefore V\,dp - s\,dT = dg$

at equilibruim: $dg_v = dg_L$

$dg_v = V^v\,dp - s^v\,dT$

$dg_L = V^L\,dp - s^L\,dT$ ⊖

$0 = \underbrace{(V^v - V^L)}_{\Delta V}\,dp - \underbrace{(s^v - s^L)}_{\Delta S}\,dT$

$\frac{dP}{dT} = \boxed{\frac{\Delta S}{\Delta V}}$ → substitute ---- ⊛⊛

$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$ → $H^v > H_L$ → ⊕

→ $V^v > V^L$ → ⊕

→ مشتق slop

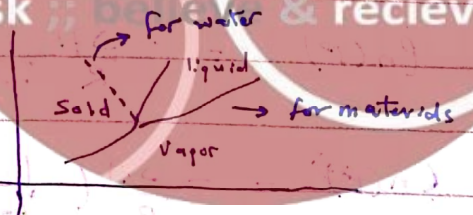
↓ in Kelvin always ⊕

In (Solid — liquid) eq:

$\Delta H_{melting}$ ⊕ $H_L > H_s$

ΔV ⊕ But for water

ΔV ⊖ → $\rho_L > \rho_s$, $\hat{v}_s > \hat{v}_L$



Derevation

No: Clausis Clapeyron Date: 23th feb

⊛ melting slop for water (—)

$\frac{\Delta s}{\Delta V}$ → clapiron eq.

classify. at eq if (solid - vapor) (liquid - vapor)

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \simeq \frac{\Delta H}{T \boxed{V^v}}$$ → substitute with ideal gas law !!

⊛ because $\hat{V}_L$ very small in compression with steam

$$\boxed{V = \frac{RT}{P}}$$

$$\frac{dP}{dT} = \frac{\Delta H}{T \frac{RT}{P}} = \frac{\Delta H}{T RT} P$$

$$\frac{dP}{P} = \frac{\Delta H}{T^2 R} dT \qquad \therefore \frac{dx}{x} = d[\ln x]$$

$$d \ln(P) = \frac{\Delta H}{T^2 R} dT$$ [clausis clapeyron eq.]

R → constant

↓ assumption

vapor ≡ ideal gas

$\hat{V}_V \gg \hat{V}_L$ or $\hat{V}_s$

(ΔH) → fxn of Temp. ?.

ψ → ⊛ assumes narrow Temp. range so $\Delta H \simeq$ constant so our integration w.r.t T

⊛ you can apply this eq (V-S) eq (L-V) eq

⊛ you can't apply for (S-L) eq

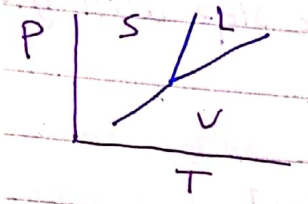
$$\int d \ln(P) = \int \frac{\Delta H}{R} \frac{1}{T^2} dT$$

$$\ln(P) = -\frac{\Delta H}{R} \frac{1}{T} + C$$ OR because $(V_S \simeq V_L)$

$$\ln(P) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) + C$$

No: Clausis Clapeyron Date: 23th - Feb - 2020

* we can apply this equation experimentally (P vapor pressure) and (Temp.)



→ then we can find (ΔH vap) → ΔS ??

slop

$$T\frac{\Delta S}{T} = \frac{\Delta H}{T}$$

$$\Delta S_{vap} = \frac{\Delta H}{T}$$

* using this equation ables us to know the phase of material.

#

Q: Trimethyl gallium, $Ga(CH_3)_3$, can be used as a feed gas to grow films of GaAs. Eshmate the enthalpy of vaporization of $Ga(CH_3)_3$ from the data of saturation pressure Vs. Temperature given in the table

T(K)	P^{sat} [kPa] →	$\ln P^{sat}$	$\frac{1}{T}$
250	2.04	0.7	0.004
260	3.3	1.2	0.0038
270	7.15	2	0.0037
280	12.37	2.5	0.0035
290	20.45	3.0	0.0034
360	32.48	3.5	0.0033
310	49.75	4.0	0.0032

From clausius - Clapeyron equation.

$$\ln P^{sat} = const - \frac{\Delta h_{vap}}{RT}$$

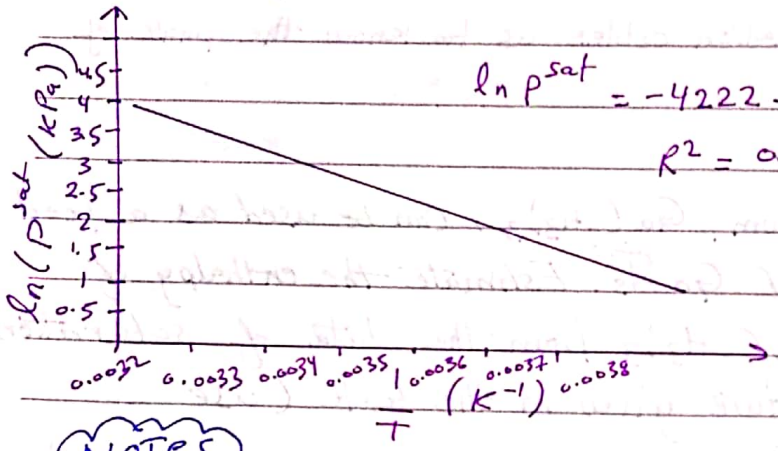
No: clausis--- Date: 23-Feb-2020
Clapeyeon

* If we plot $\ln P^{sat}$ vs T^{-1} the slop will give $-(\Delta h_{vap,\ Ga(CH_3)_3}/R)$.

$$\frac{-\Delta h_{vap}\ Ga(CH_3)_3}{R} = -4222.1\ [K]$$

→ Its unit depends on R's unite

$\rightarrow \Delta h_{vap} = 35.1\ [kJ/mol]$. constant



$\ln P^{sat} = -4222.1\ T^{-1} + 17.556$

$R^2 = 0.9973$.

NOTES

* How to control P in lab? by weights

* If (ΔH) in [kJ/kg]
→ conversion → molecular weight → for common elements

Q: estimate ΔS in that range ?!

$\Delta S = \frac{\Delta H}{T}$ → at which T ??

$T(K) \approx 280\ K$

$\Delta S \approx \frac{35.1 * 10^3\ J/mol}{280} = 125.3\ J/mol\ K$

Q: the equation given and find: ΔH, or phase diagram

Q: ΔH is given find: Vapor P or Temp

No ..... Date: 23 - Feb - 2020

* constrains to apply first and second law of thermodynmics?
assumtions: ① neglicate electrical, nuclearal, magnatic, Surface Tension] fileds

but when you apply 1st and 2nd law of thermodynmics on (nanoparticle)
we can't neglict surface tension.
↓ size of particle ↑ surface tension

Henery's law and Raoult's law
25/ Feb
* Henery's law
* Rault's law
* limition of Roult's law

For a system composed of C component and P phases the following crateria must be simultaneously apply.

1. Thermal equilibrum $T^{(1)} = T^{(2)} = T^{(P)}$
2. Mechanical eq. $P^{(1)} = P^{(2)} = P^{(P)}$
3. Chemical eq. $f_i^{(1)} = f_i^{(2)} = f_i^{(P)} \quad i = 1, 2, 3, \dots, C$

$\mu_i^{(1)} = \mu_i^{(2)} = \dots \mu_i^{(P)} \quad i = 1, 2, 3, \dots, C$

↓ chemical Potential ≡ driving force

for mass transfer ≡ concentration difference

If there is a driving force there is not eq.

for mass transfer ≡ Chemical potential main driving force

f and μ for a component ≡ G. (gibbs energy)

Henery's law
No: Raoult's law Date: 25th - Feb - 2020

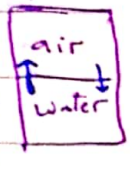
Q: Composition of air and water at eq. at 20°C = 68°F 1.00 atm Pressure.

	Gas phase	liquid phase
Mol fraction water	0.023	0.999985
Mol fraction Oxygen	0.205	5×10^{-6}
Mol fraction Nitrogen	0.772	10×10^{-6}
Sum of mol fraction	1.00	1.00

NOTE: This treats air as 21% oxygen, 79% nitrogen, ignoring its other minor species

*(Iso-fugacity condition)

$f_{N_2}^{(air)} = f_{N_2}^{(w)}$ $f_{O_2}^{(air)} = f_{O_2}^{(w)}$ $f_{H_2O}^{(air)} = f_{H_2O}^{(w)}$



↳ chemical equilibroim

NOTE: Ideal vapor phase → f = mole fraction × total Pressure

$T^{(air)} = T^{(w)}$ → Thermal eq

$P^{(air)} = P^{(w)}$ → Mechanical eq] ISdown ✓

NOTE: we can make 3 material Balance → 3 material

#gas: $f_i^{(gas)} = y_i P$ → Ideal gas

$y_{H_2O} P$

$y_{O_2} P$

$y_{N_2} P$

#liquid: → (مادة مركزة بنباتي liquid phase) → using Roult's law

→ (تراكيز قليلة أقل من $\frac{1}{1000}$) → using Henery's law

Henery's law
Raoult's law

No. Date: 25th - feb - 2020

Raoult's law :

$f_i^{(\text{Liquid phase})} = x_i \; P_i^{vap}$

$y_{H_2O} \; P = x_{H_2O} \; P^{vap}_{H_2O}$ → anton aq. → يعتمد على إذابة وشاوين هي موجودة

NOTE : O_2 and N_2 not too soluble in water so we can't apply raoult's law

* Sparingly soluble ↓↓↓ قليلة الذوبان = henery's law

Henery's law :

$f_i^{(liquid)} = x_i \; H_i$ → henery's law constant

* Henery's law constant → fxn of Temp., Its unit is (bar)
* Henery's law constant depend on :
  ① ON Temperature of component
  ② ON Solvent that component in

Ex : $H(O_2 \text{ in } H_2O) \neq H(O_2 \text{ in acetone})$; (Solvent & solute)

H_2O = solvent $\quad N_2 / O_2$ → solute

my equations from Henery's law →
$y_{O_2} P = x_{O_2} H(O_2 - H_2O)$
$y_{N_2} P = x_{N_2} H(N_2 - H_2O)$
→ you can find in tables

my eq. from Raoult's law → $y_{H_2O} P = x_{H_2O} P^{vap}_{H_2O}$
P known, $P^{vap}_{H_2O}$ known

⇒ 6 unknown → you have 3 eq.

No: Henery's law / Raoult's law Date: 25th Feb 2020

$\sum y_i = 1$ $\quad y_{O_2} + y_{H_2O} + y_{N_2} = 1$ → for vapor

$\sum x_i = 1$ $\quad x_{O_2} + x_{H_2O} + x_{N_2} = 1$ → for liquid

eq 5,4

$\%\ O_2 : \%\ N_2 \rightarrow \frac{21}{79}$ — eq 6

Now you can solve the equation simultaneously

= system of linear equation

$$\begin{bmatrix} & \end{bmatrix} \begin{bmatrix} \end{bmatrix} = \begin{bmatrix} \end{bmatrix} \qquad Ax = b$$

$A^{-1} b = X$ ✓

IN (AIR) (Gas phase)

Mol fraction of $O_2 \rightarrow 0.205$ ↓ (dissolving in water)

$N_2 \rightarrow 0.772$ ↓

IN WATER (LIQUID phase)

Mol fraction → $O_2 = 5 \times 10^{-6}$ (saturation)

→ $N_2 = 10 \times 10^{-6}$

Solubility N_2 in water > solubility O_2 in water

solubility $N_2 : O_2$ in air ≈ 4:1 ?? Why

" $N_2 : O_2$ in water ≈ 2:1

↑ soluble in water ↓ henery's constant

if $\%\ N_2 = \%\ O_2$ in air → solubility of $O_2 \gg N_2$ in water !!

Henery's law
No: Raoult's law Date: 1st - March - 2020

* Henery's law constant + vapor pressure → depending on Temp.
* H_i for gases ↑ Temp ↑ Solubility gases ↓
* Solubility $\propto \frac{1}{H_i}$

* $y_i P = x_i H_i$
  (H_i → bar (Pressure unite))

Gas	H_i (bar) for water (solvent) at 25°C (Temp.)	
C_2H_2	1342.2	→ (ethyne) mo soluble gas in water at 25°C * using in welding
N_2	87365.0	→ least soluble gas in water @ 25°C

Q: The highest concentration of CO_2 in water @ 25°C ??
* concentration ≡ solubility

$y_i P = x_i H_i$ → so; $x_i = \frac{y_i P}{H_i} = \frac{1 * 1}{1651.9}$ (CO_2 / water)

$x_i = 6 \times 10^{-4}$ mol CO_2 / mol solution

⇒ $\frac{mg}{L}$ (ppm) $= 6\times10^{-4} \frac{mol\ CO_2}{mol\ sol} \left| \frac{44\ g\ CO_2}{1\ mol\ CO_2} \right| \frac{mol\ sol}{18\ g\ sol}$

اعتبرت sol هي water لأن كمية CO_2 قليلة جداً وتركيزه صغير جداً.

$= 6\times10^{-4} * \frac{44}{18} * \frac{g\ CO_2}{g\ sol} = 1.48\times10^{-3} \frac{g\ CO_2}{g\ sol}$ → to convert mg

(ppm) $= 1.48\times10^{-3} \frac{g\ CO_2}{g\ sol} \left| \frac{1000\ mg\ CO_2}{g\ CO_2} \right| \frac{g\ sol}{10^{-3}\ L} = 1480$ ppm (convert to L; water $\rho = 1$)

Is solution acidic or Basic? Acidic. $CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$ (Carbonic acid)
* Application on solution (gas – liquid (water))
* Most Acids are gases dissolved in water

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$HF_{(g)} + H_2O \rightarrow HF_{(aq)}$

$HCl_{(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)}$ highest concentration 36% #

hydrogen chloride — hydrochloric acid

it's not acid

$H_2O_{(l)} + NO_{2(g)} \rightarrow HNO_3 + NO$ solubility 50%

$NO_{(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)}$

$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$ solubility >100 (draw)

↳ (captured plants) → ...

$P_2O_{5(g)} + 3H_2O_{(l)} \rightarrow 2H_3PO_{4(aq)}$

* Natural gas

CH_4 + another materials → H_2O, CO_2, H_2S → how to remove from natural gas + or from petrolum

* To remove CO_2 from natural gas or H_2S?

⇒ Find solvent that CO_2 has high solubility in it??

Ethanol Amines

Why?? because such compounds react chemically not just dissolve physically

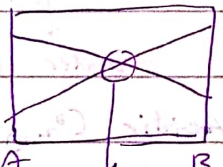
CO_2, H_2S + ethanol Amines → ↑ solubility

Ionic liquids Ions without water @ 0°C It's vapor pressur=0

It's still in its phase even with heating

Solute → vapor phase solvent → DES

or **DES**



eutechic point : lowest melting point of a mixture

Ionic without water : electrostatic interactions → solutes removing

No. Raoult's law Date: 3rd March - 2020

* solubility → henery's law.

* Raoult's law ≡ gases Ideal

$y_i P = x_i P_i^{vap}$

Fugacity Ideal gas or Ideal solution

distribution coeff. ≡ No unite

$k_{(i)} = \frac{y_i}{x_i}$ → mol fraction in vapor phase

x_i → mol fraction in liquid or solid phase

Solution خليط مادة معينة في

k → >1 → المادة تتركز → vapor phase → أكثر → liquid phase ↑ سخن

k → $=1$ → NOT prefer → NOT easy to separate

k → <1 → solubility in liquid phase > vapor phase ↓ برد

* Separation : for example : distillation : most prefer

↳ simple, available, NOT down stream processing

بطلعلك عادة صابرة مثل ما بدك، فش فوق أعلى وراه أشي

* ex: for down stream processing → فصل الكافيين سبرتاي

لـ solid ← ما بقى / أعلى distillation بطريقة صابرة

* Relative volatility : $\alpha_{1,2} = \frac{k_1}{k_2} = \frac{(y_1/x_1)}{(y_2/x_2)}$

لـ مقارنة بين مادتين

index انتبه لـ ← $\alpha_{(2,1)} = \frac{k_2}{k_1}$

α_{ij} ← (+) (أكبر) ← $(0, \infty)$

>1 volatile 1 > volatile 2 ; If It's index $\alpha_{(1,2)}$

$=1$

<1 volatile 2 > volatile 1 → distillation

vapor phase ≡ distillate stream } in distillation process

liquid phase ≡ bottom stream

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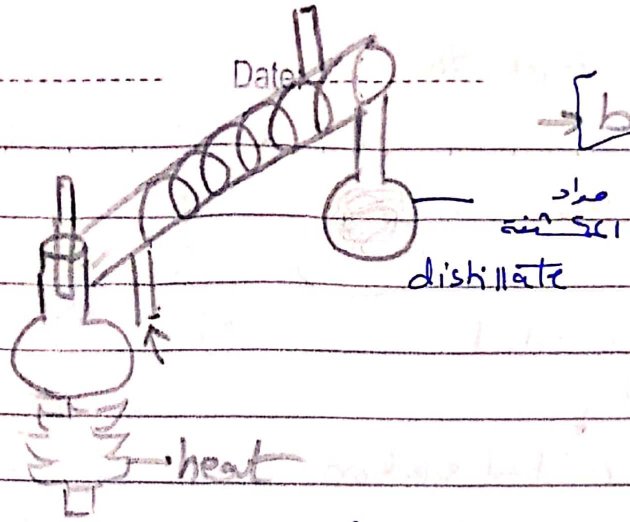
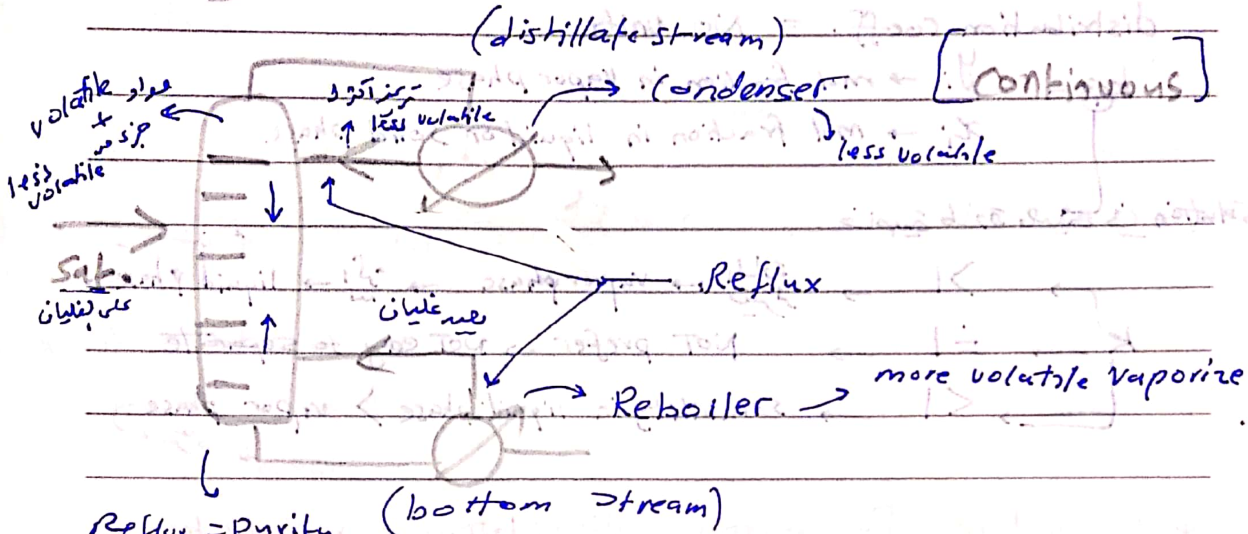
→ [batch]



[continuous]



Reflux = Purity

* $\alpha_{1,2} > 1$ $\frac{k_1}{k_2} > 1$ → k_1 distillate stream
  → k_2 bottom stream
* $\alpha_{1,2} < 1$ → عكس
* $\alpha = 1$ = impossible ; ~~normal distillation~~
  → [illegible] مادة ثانية
  ↓ لفصل المواد
  $\alpha \cong 1$ →

Representation of VLE Data.

No: Date: 8th - Mar. 2020 <3

* $0.95 \leq \alpha_{1,2} \leq 1.05$ → you can use distillation
* $\alpha_{12} > 1$ → component 1 → distillate stream
  $\alpha_{12} < 1$ → component 1 → bottom stream or residue
* $\sum$ mole fraction in each phase $= 1$

Note: * if there are three component → 3α can be measured [α_{12}, α_{23}, α_{31}]
one at least of them >1, and one at least <1

* $\alpha_{1,2} \neq \alpha_{2,1}$ → It depends on what index Φ needs.
* Indexces in Φ

Exam.

* phase digram → binary system ≡ (y, x) ...
* pure component:
  P vs T , T vs V , P vs V ... There is not a composition

* T-xy [T vs x → mol. frxn → liquid phase; y → mol. frxn → vapor phase] at constant P
* $P_{x,y}$ [P vs x, y] at constant T

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* +ve deviation > Raoult' Law
* -ve deviation < Raoult' law

Raoult's law → Ideal

* Raoult's law → Vapor = Ideal gas mixture
  liquid = Ideal soln.

Ideal Soln ← system
or
non-Ideal soln ←

3 constrains

Note:

* non-Ideality in liquid phase >> vapor phase ??
  vapor phase has $\underline{f}$ much smaller, so there aren't interaction between the molecules.
  liquid phase $\underline{f}$ → much larger ; small distances between molecule → interaction → attraction
  → Repulsion

Shap
Size
Chemical interaction (specific interaction)

→ liquid phase → component of liquid mixture → Shap, Size, Specific interaction → functional group

To have Ideal solution →
Size
Shape
specific interaction

Determine which is Ideal or non-Ideal of the following ??

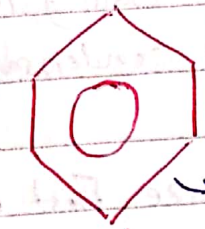
No: Date:

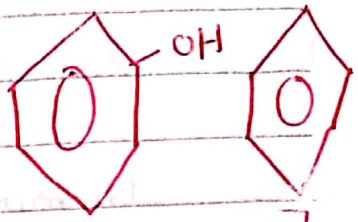
* n-hexane
n-heptane
[Ideal soln]

* n-hexane
n-hexanol
[non-Ideal]
nonpolar → polar
specific chemical interaction

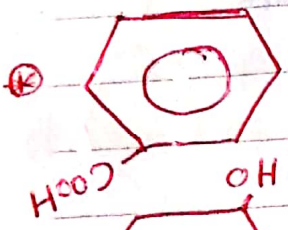
* n-dodecane
n-hexanol
[non-Ideal soln.]

* n-hexane
n-dodecane
[non-Ideal (size)]

* 
C_6H_6
→ Ring
n-hexyne → chain
[non-Ideal]

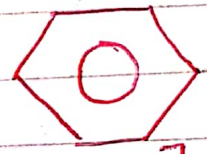
* 

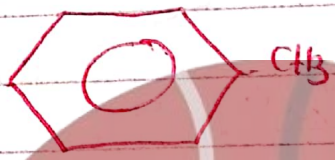
[non-Ideal]
specific chemical interaction

* 

[non-Ideal → specific chemical]

Shape, size, Chemical interaction
↓
bond → aromatic
→ triple

* 



[non-Ideal], size

* Ideal soln. → 3 chrateria applied

* $y_i P \phi_i = \gamma_i x_i P_i^{vap}$
(ϕ_i fugacity coefficient)
γ_i → to express non-Idealit
gas mixt. (activity coefficient)
Ideal = 1
non ideal ≠ 1
$\gamma_i > 1$ → + deviation
$\gamma_i < 1$ → − deviation
$\gamma_i = 1$ → Raoult's law

No:- VLE Data Date:- 8th Mar-2020

[0 — 1] → مكان التقاء ال curves

0 — 1

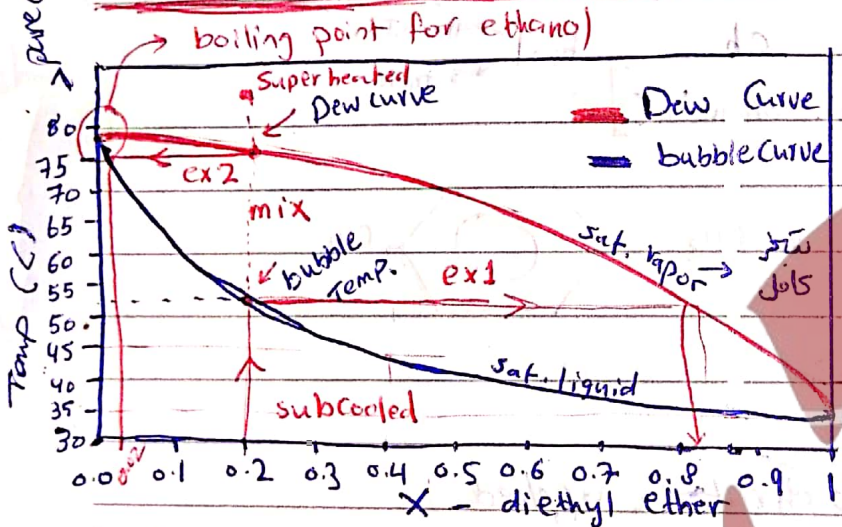
pure component limit

$[x_1 = 0, x_2 = 1]$ boiling Temp for liquid or condesation Temp for vapor ≡ the same

$[x_1 = 1, x_2 = 0]$ boiling Temp and condensation Temp

In mixture → raporize First more volatile
→ conden sate First Less volalite

10th March 2020



④ $T\begin{bmatrix} x_1 \\ y_1 \end{bmatrix}$ component ①

diethyl ether (1) ethanol (2) system

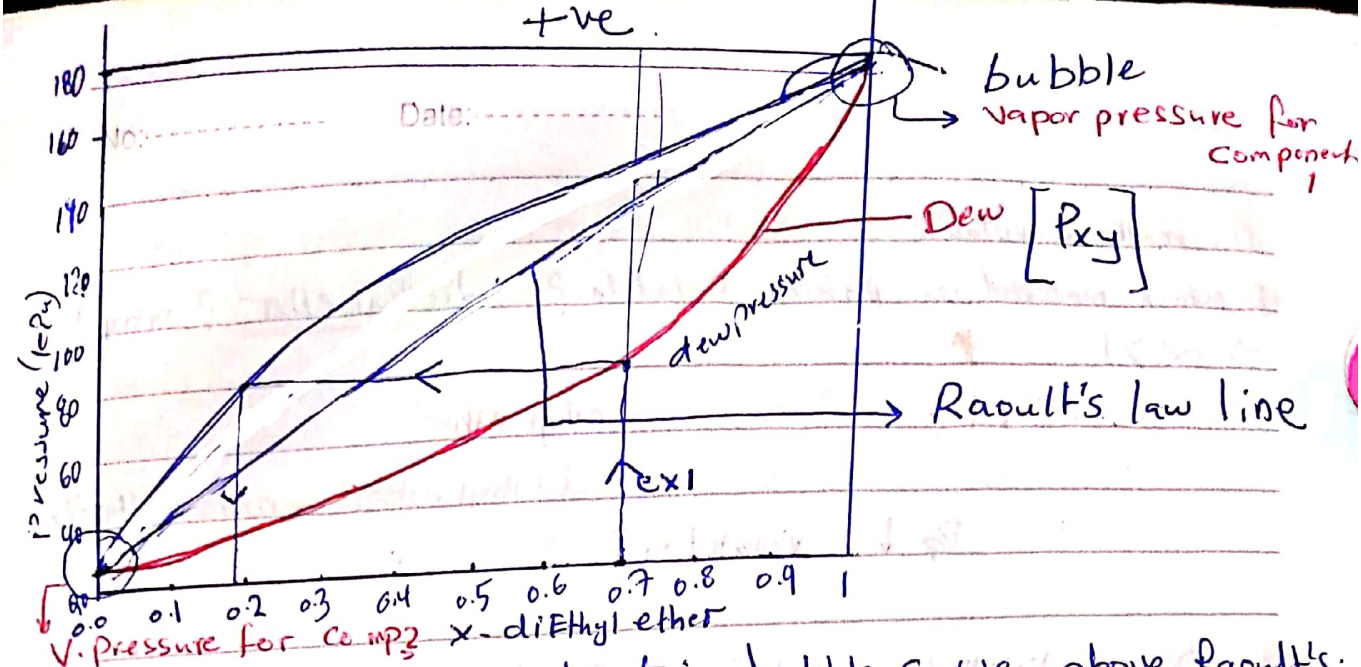
Txy @ 101.325 kPa → 1 atm

(+ve) deviation → bubbl curve (Pxy) above Raoult's law line

ex @ $x_1 = 0.2$

bubble Temp: Temp where the first bubble of vapor is formed when healting a liquid consisting of two or more components

more volitile → vaporise more than less volatile component as Temperature raises.



V. pressure for comp 2

Pxy @ 30°C → (+ve) deviation bubble curve above Raoult's.

↳ antonie eq → Find vapor pressure for ethanol and diethyl ether → two point → Curve ✓

* Pxy → bubble curve above Dew curve
  Txy → bubble curve below Dew curve

* Quality → bubble curve = 0
  ↳ Dew curve = 1

* ether [C-O-C] ethanol [COH]
  functional group not the same
  chemical specific
  system is not ideal

ex:1 and ex: 2 based on Txy curve :

ex 1: suppose mixture $x_1 = 0.2$ [diethylether]
$P = 101.325$ (constant in Txy)
$[y_1]$ at equilibrum with that liquid ?

at eq → bubble curve → [illegible]

$y_1 \simeq 0.7$ Txy [illegible] for diethyl ether

* $K_1 = \frac{y_1}{x_1} = \frac{0.7}{0.2} = 3.5$ * $K_2 = \frac{y_2}{x_2} = \frac{0.3}{0.8} = 0.375$

$\therefore \alpha_{12} = \frac{K_1}{K_2} = \frac{3.5}{0.375} = 9.33$

So,

⊛ which material is more volatile? diethyl ether ? why?

→ $\alpha > 1$

→ Boiling Temp 78 °C for ethanol

" " 35 °C for diethyl ether → more volatile

Bp ↓ volatility ↑

⊛ Does distillation column efficient separation method for such mixture? [yes]

→ $0.95 \leq \alpha_{1,2} \leq 1.05$ → not prefer distillation column

$\alpha_{1,2} = 9.33$ ✓✓ → distillation column suitable

⊛ $\alpha = 1.1 , 1.2$ → (distillation) J1 يمكن فصل

⊛ Bubble Temp? ≃ 55°C

ex2: $y_1 = 0.2$ (vapor) Find x_1 that is at equilibrum? حالة توازن

$x_1 = 0.02$

⊛ $K_1 = \frac{0.2}{0.02} = 10$ ⊛ $K_2 = \frac{0.8}{0.98} = 0.81$

$\therefore \alpha_{12} = K_1/K_2 = 12.25$

* NOTE: α, K are fxn of composition

non-Ideal sup → K, α → aren't const.

⊛ Dew point? 74 °C

⊛ Dew point → قطرة ← droplet → Liquid تتكون

⊛ droplet → less volatile تتكثف أولاً

=

No: ---------- Date: ----------

bubble point → more volatile

* Pxy → on Pxy

① bubble curve → indicator if our mixture applies Raoult's law or not

② vapor pressure ↑ volatile ↑

✱ Prove that Raoult's line comes from Raoult's eq.?

$$y_i P_{total} = x_i P_i^{vap}$$

$$\left.\begin{aligned} y_1 P &= x_1 P_1^{vap} \\ y_2 P &= x_2 P_2^{vap} \end{aligned}\right] \oplus$$

$$(y_1 + y_2) P = x_1 P_1^{vap} + x_2 P_2^{vap}$$

for binary system = 1

$$P = x_1 P_1^{vap} + \underbrace{x_2}_{(1-x_1)} P_2^{vap} \rightarrow P = x_1 P_1^{vap} + (1-x_1) P_2^{vap}$$

$$P = P_2^{vap} + (P_1^{vap} - P_2^{vap}) x_1 \rightarrow P = a + bx_1$$

↓ intercept عند التقاطع

P_2^{vap} → constant → T constant

$$y_1 P = x_1 P_1^{vap} \rightarrow k_1 = \frac{P_1^{vap}}{P}$$

$$y_2 P = x_2 P_2^{vap} \rightarrow k_2 = \frac{P_2^{vap}}{P}$$

k_1 and k_2 fxn of T and P

$$\alpha_{12} = \frac{k_1}{k_2} = \frac{P_1^{vap}/P}{P_2^{vap}/P} \rightarrow \text{fxn of } T \rightarrow \text{Raoult's law}$$

No:---------- Date:----------

* you don't improve distillation column by changing Pressure From Raoult's law, change Temp!

(ex): From Pxy curve:

$y_1 = 0.7$

x_1 at eq $= 0.175$

$k_1 = \frac{0.7}{0.175} = 4$

$k_2 = \frac{0.3}{0.025} = 0.36$

$\alpha_{1,2} = \frac{4}{0.36} = 11$

Compare: $\alpha_{12} = 9.3$ (55°C) $\quad \alpha = 11$ (50°C)

$\alpha_{12} = \frac{P_1^{vap}}{P_2^{vap}}$ → P^{vap} كبير من نفس P^{vap} كبير

diethyl ether, ethanol