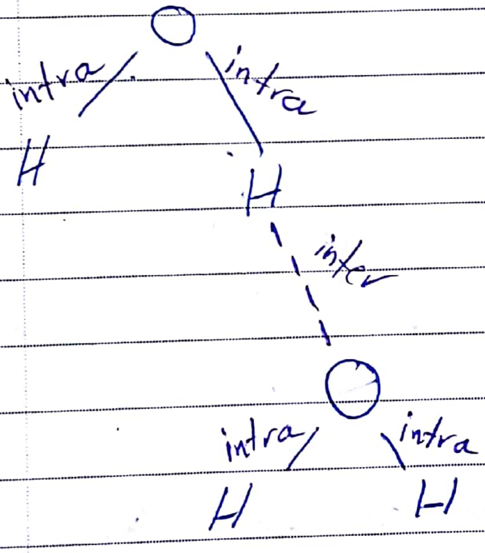
No. Chapter 12

Intermolecular forces (inter molecular)

* inter molecular force => forces between different moleculars

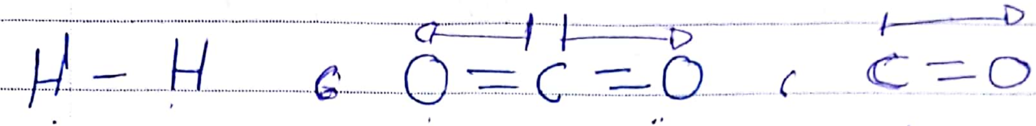
* intra " " => forces between atoms within a moleaular (chemical bonds)

what determine the physical state of a matter in the intermolecular interaction



930 kJ/mol to break all intra
41 kJ/mol to " " inter

dipole moment (Polarity)



non-polar — non-polar — Polar.

C − H

non-polar

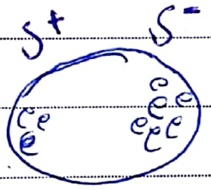
* لتحديد اذا كان المركب قطبي أولاً نجد الفرق بين كهروسلبية الذرات المكونة له

(4 - 2) ⇒ ionic

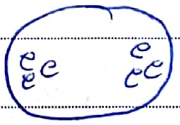
(2 - 0.3) ⇒ polar

less 0.3 ⇒ non-polar

* الجزيء القطبي يعطي وجود e^- بجهة أكثر من اخرى



polar molecule



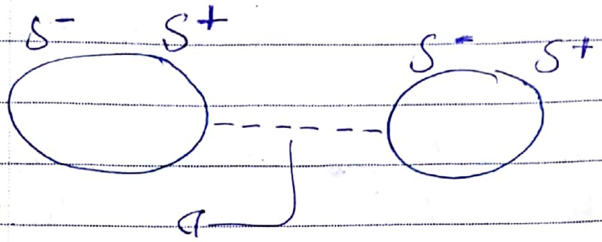
non-polar molecule.

Types of intermolecular interaction.

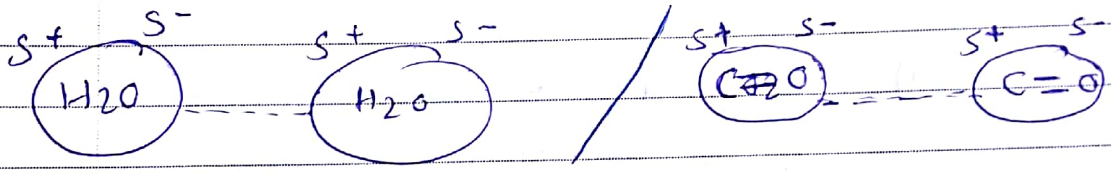
① Dipole - Dipole force.

interaction between two polar compound.

No.



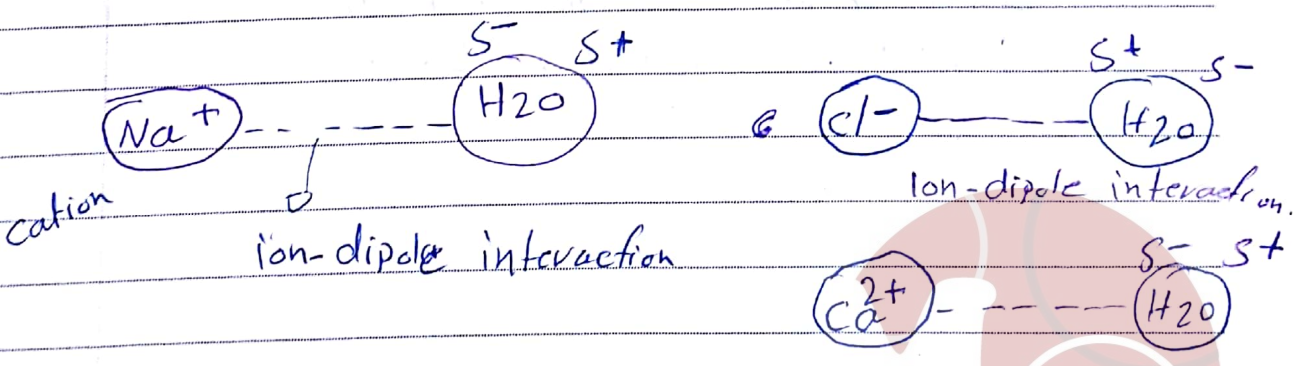
important
* inter molecular force
* electrostic force.
قوى * dipole - dipole.



* Strenght of the intermolecular force ~~d~~depends on ⇒ the polarity of the interacting molecules

* قوة $\boxed{H_2O}$ أكبر من قوة $\boxed{CO}$ بدلالة درجة الغليان والتجمد أو اللزوجة ترتبط بشكل طردي
بينما الضغط البخاري بشكل عكسي.

② Ion- ~~polar~~ dipole force
interaction between Ion and polar compound.



factors affecting ion - dipole interaction

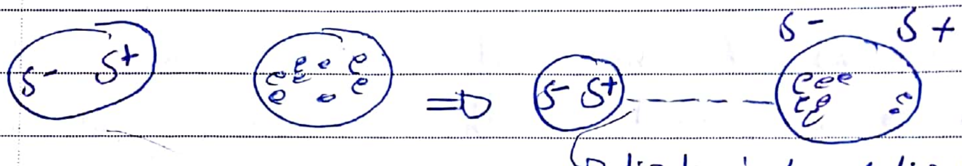
عكسي 1- Size of ion (نصف) } → charge density = $\frac{\text{charge}}{\text{volume}}$.

طردي 2- charge on the ion }

طردي 3- polarity of other molecule.

③ Dispersion forces

a) $\underbrace{\text{dipole}}_{\text{Polar compound}}$ - $\underbrace{\text{induced dipole}}_{\text{non-polar compound}}$ interaction.

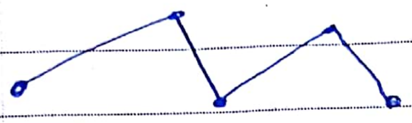


بسبب الكثافة الكبيرة تنتقل e⁻ للقطب الأقرب

→ dipole - induced dipole interaction.

Factors affecting interaction :-

① Polarity of the polar Compond
② number of e⁻ in the non-polar compand.
③ ease of movement of the e⁻



H_2O

H_2O

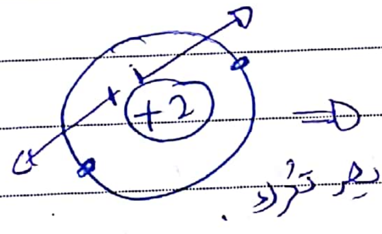
الرابطة اقوى لان
الروابط الثنائية أضعف
من الاحادية فتنكسر بسهولة وبالتالي تتحطم بسهولة اكثر.

b) London forces ⇒ interaction between two non-polar compound.

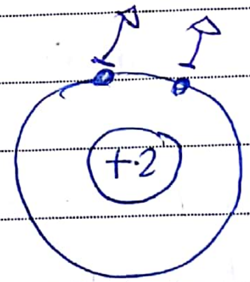
درجة غليانه.

N_2 ⇒ N≡N liquid ~~at~~ -196C°

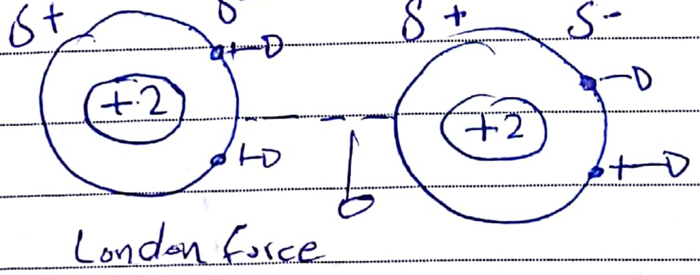
He liquid ⇒ -269° C



يصير تردد.



ذرة He احيانا تكون مستقطبة على وقت طويل.
ولكن لحظة تكون غير مستقطبة.



London force

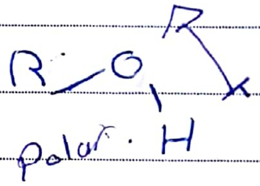
عند تساوي عدد الالكترونات بالمركبات أو تساوي الحجم يكون قوة
London. أكبر من dipole-dipole

factors affecting the London forces

① number of e⁻ (mass the compound)
② polarizability (الاستقطاب)

قوي CH_3CH_2OH (Polar) ① dipole-dipole.
(OH group) ② London. (78° درجة غليان)
CH_3OCH_3 (~~non~~-polar) London (34 C°)

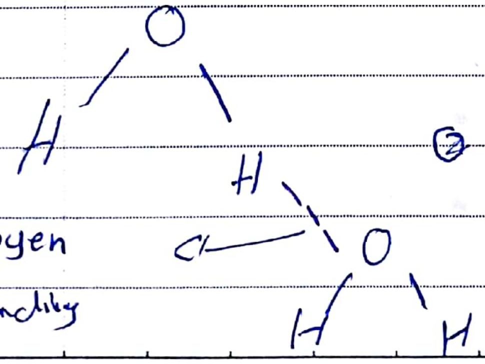
.... لكن قطبية ضعيفة

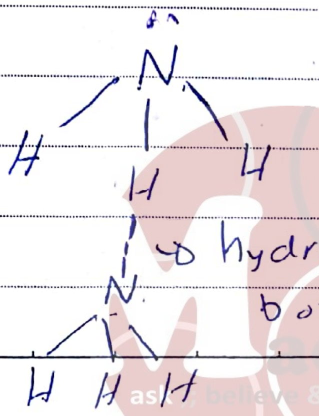


Hydrogen bonding.

is a special case of dipole-dipole intraction where $\boxed{H}$ atom comes between two atom of [N, O, F]

Hydrogen bonding

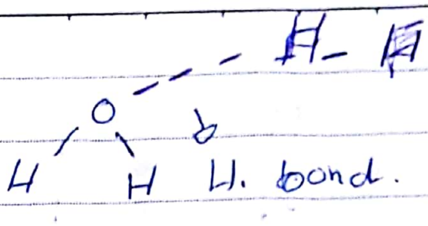


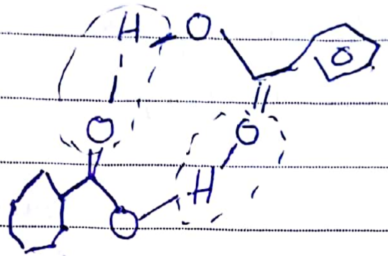


→ hydrogen bonding

No.

H − F - - - H − F
H. bond





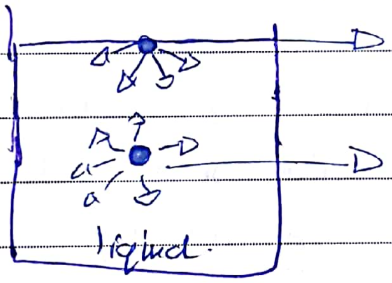
تعمل رابطتين هيدروجينيتين.

من الممكن أن تكون ذرة H متورطة بأكثر من رابطة هيدروجينية.

Properties of liquids

① Surface tension التوتر السطحي.

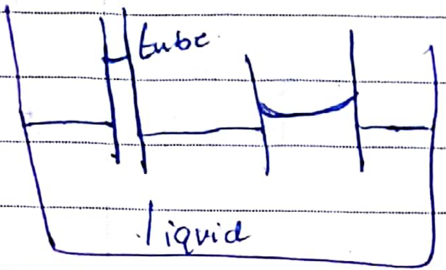
يؤدي الى أن السوائل بشكل عام تتكور بحيث يكون لها أقل مساحة سطحية.



→ net force (downword) → المسبب وراء التوتر السطحي.

→ no net force.

* magnetude of surface tension : amount of energy required to stretch the surface of a liquid by unit area. unit ⇒ $\frac{J}{area} = \frac{J}{m^2}$



two types of intreaction

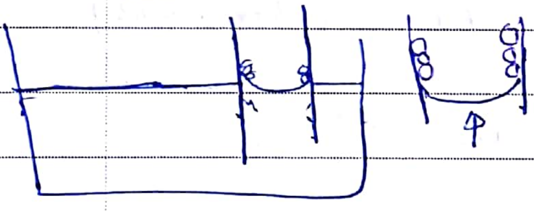
1. between liquid particols
(cohesion)

2- " " " and the wall
s of the tube (adhesion)

* if adhesion = cohesion then the liquid level will not change.

* if coh > adh the level will lower

* if ~~coh > adh~~ adh > col the " " rise.



* قوة التلاصق ترفع ذرات السائل
والتوتر السطحي يرفع بقية السائل -
بحيث تبقى المساحة أقل ما يمكن
ومن ثم قوة التلاصق تعيد رفع الذرات وتبقى العملية هكذا حتى يتساوى
الجاذبية مع التوتر السطحي.

inter $\xrightarrow{\text{طاقة}}$ surface

نقصان [illegible] $\xrightarrow[\text{طاقه}]{}$ inter

No.

Viscosity (اللزوجة)

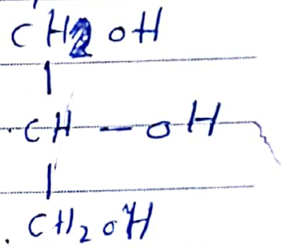
* is a measure of fluid's resistance to flow

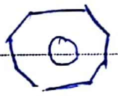
* as intermolecular interaction increases viscosity will increase.

* The viscosity of liqued usually decreases as temp increases.

* H_2O > CH_3OH

الماء أكثر لزوجة لأن الروابط الهيدروجينية أقوى في الماء
حيث يوجد ذرتين (H) في الماء.





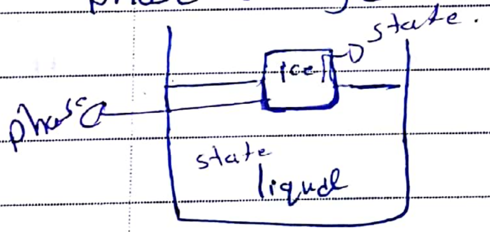
الأضعف

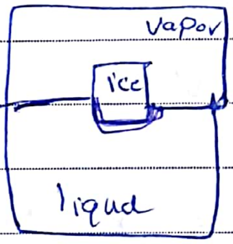
وجود لندن كقوة فقط

الروابط اقوى
بسبب 200° C

وجود OH روابط هيدروجينية بالإضافة إلى قوة لندن بسبب وجود عدد الكربون CH_2 و CH

phase change.





3 state.
2 phase.

phase => part of a system in contact with other parts with well defined boundary (محدد)

phase change: transformation from one state into another through a phase.

No.

Liquid $\rightarrow$ Vapor vaporization

$V \rightarrow L$ condensation

$S \rightarrow L$ melting / fussion

$L \rightarrow S$ freezing

$S \rightarrow V$ sublimation

$V \rightarrow S$ deposition

تتكسر كل الروابط $L \rightleftharpoons V$ endotheromic ΔH_v

عدد محدود من الروابط $S \rightleftharpoons L$ // للاتجاه الأمامي ΔH_f

تتكسر كل الروابط $S \rightarrow V$ // ΔH_s

$$\Delta H_s > \Delta H_v > \Delta H_f$$

$$\Delta H_s = \Delta H_v + \Delta H_f$$

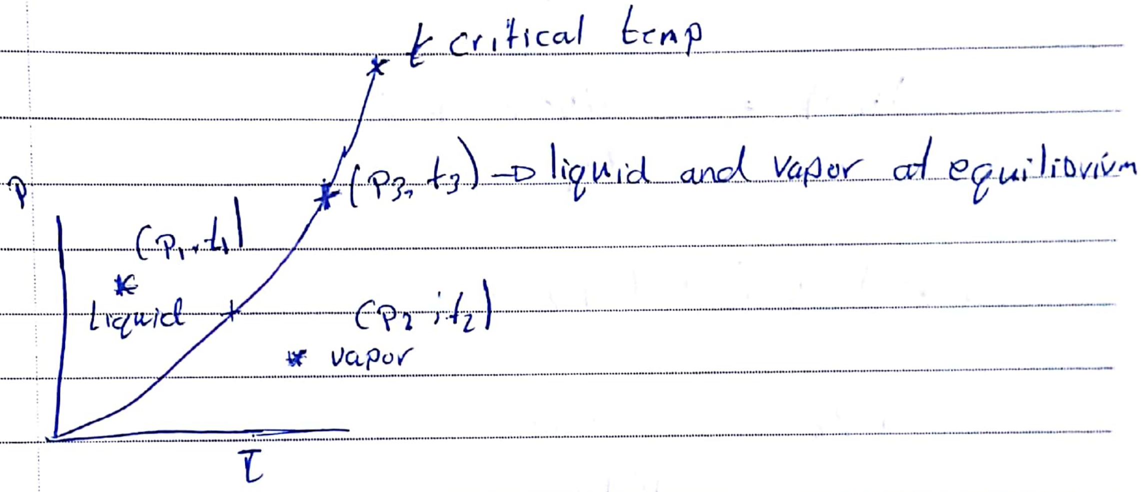
لأنها تعتمد على الكمية
intensive properties

enthalpy of vaparization ΔH_v $\left(\frac{KJ}{mol}\right)$
$\rightarrow$ energy required to completly vaporize one moll of liquid to gas

$$\boxed{P = \frac{-\Delta H_v}{RT} + C}$$ $\rightarrow$ clausius - clapyron equation

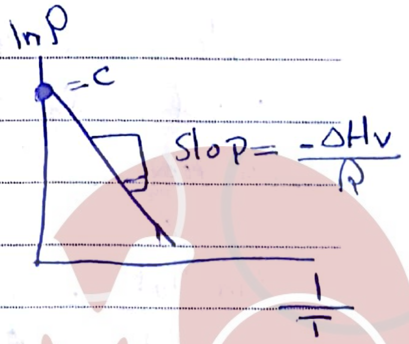
P => vapor pressure ,
R => gass constant.
T => Temp (K)

طردي
العوامل التي يعتمد عليها : ① درجة الحرارة ② نوع السائل.
الروابط الضعيفة = اللي بتعمل intermolecular interaction ← $\boxed{V.P}$



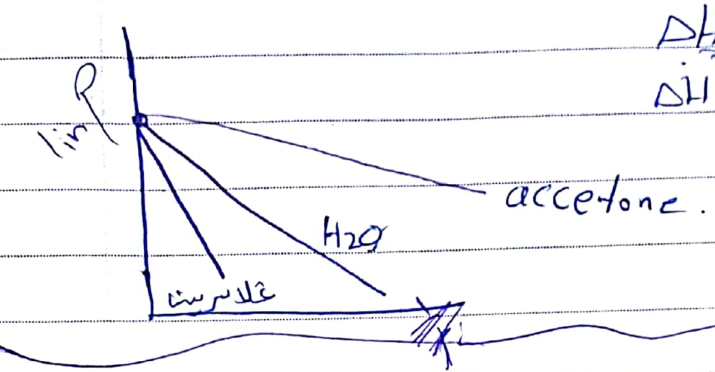
Critical tem => is the temp where the gas canot be liquified by compression (at critical temp or above the state of the matter is gas)

$$\underbrace{\ln P}_{y} = \underbrace{\frac{-\Delta H_v}{R}}_{\text{Slop}} \underbrace{\frac{1}{T}}_{X} + \underbrace{C}_{\text{intercept}}$$



No.

علاقة طردية



ΔH → slop

ΔH → (علاقة طردية) Intermolecular

المركب الذي له أكبر ΔH يكون
له أكبر ميل

Case 1 : T_1 and P_1

$$\ln P_1 = \frac{-\Delta H_{vap}}{R T_1} + C$$

Case $\boxed{2}$: T_2 and P_2

$$\ln P_2 = \frac{-\Delta H_{vap}}{R T_2}$$

$\boxed{1-2}$ → $\ln P_1 - \ln P_2 = \frac{-\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

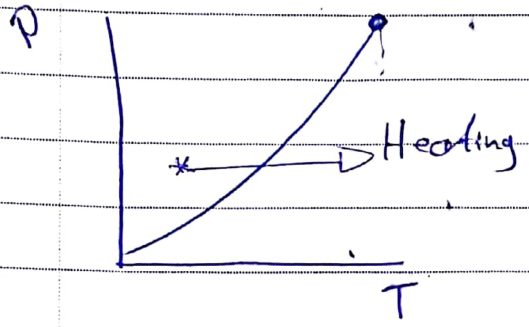
$$= \ln \frac{P_1}{P_2} = \frac{-\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

example. → CH_3CH_2OH has V.P = 401 torr at 18°C what is the V.P at 29°C. given that $\Delta H_v = 26\ kJ/mol$

Soluction.

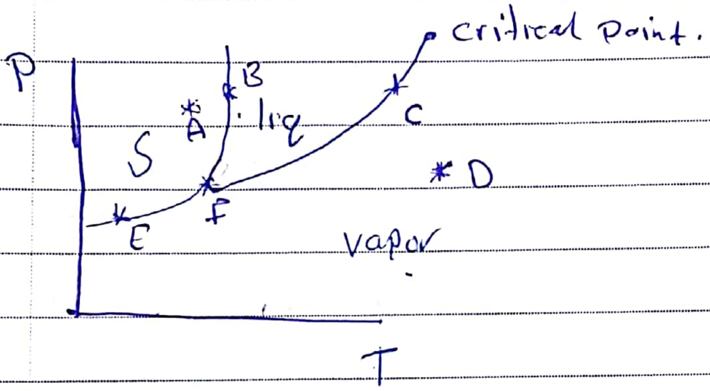
$$\ln \frac{401}{P_2} = \frac{-26\times10^3}{8.314}\left(\frac{1}{273+18} - \frac{1}{273+29}\right)$$

$P_2 = 593$ torr



phase digram

Summarize the conditions under which a substance exista as solid, liquid and gas.



B : $S \rightleftharpoons L$ equilib

C : $L \rightleftharpoons V$ "

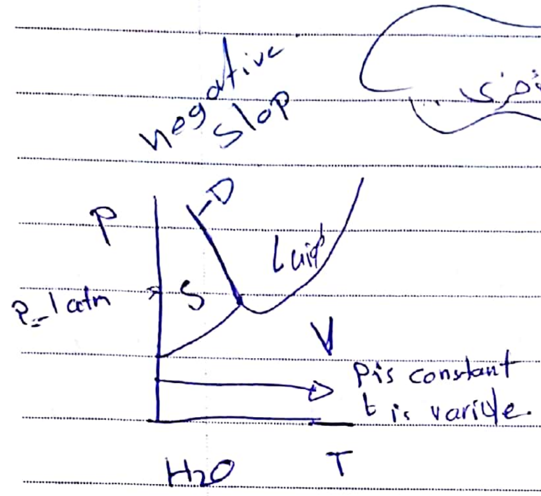
D: vapor

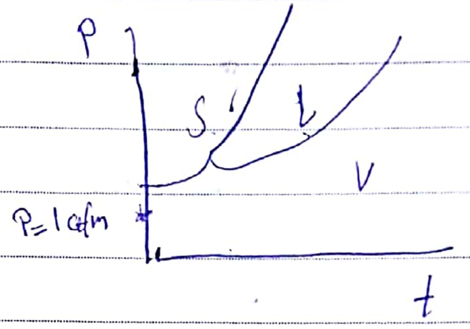
E: $S \rightleftharpoons V$

F: $S \rightleftharpoons L \rightleftharpoons$ triple point.

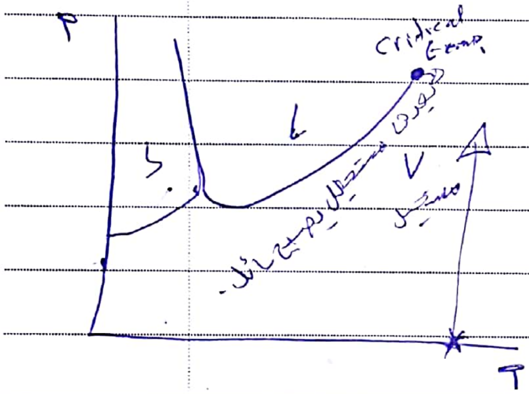
No.

كثافة الثلج أقل من الماء لانه عكس السوائل الأخرى





الذي يحصل عادة انه بالرغم من
انخفاض الحرارة الضغط انخفض



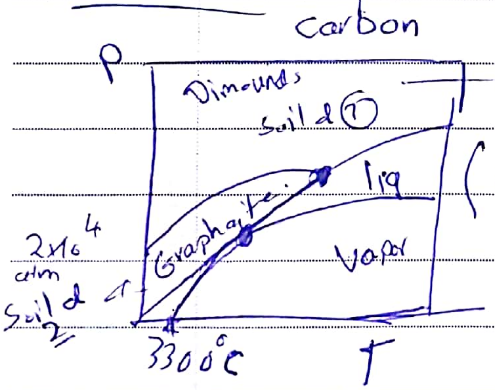
density = $\frac{\text{mass}}{\text{Volum}}$

* density of water
V > S > liquid.

phase chages by
increasing the pressure
V then S then Liquid.

example.

carbon



→ highest density

(• c •) ⇒ triple point (نقطة الالتقاء بين ثلاث)

Chapter 13

Solvation ⇒ Homogenous of solvent and solute(s)
substance exsit in larger quantites ↵

Solvent	Solute.	exaple.
Solid	Soild.	alloys.
Liqued	liqued.	Spirits (السبرتو)
liqued	gas	Soda
gas	gas.	air
Soild	gas.	Hydrogen. on pallodium.

amount of Solute in Solvent

1- unsaturated (Small anount of Soluate) $K_{sp} > [\ ][\ ]$
2- Saturated Soluation (contain max capacity of Soluate) $K_{sp} = [\ ][\ ]$
3- Supersaturated (continus soluate more than its capacity) (special case) $K_{sp} < [\ ][\ ]$

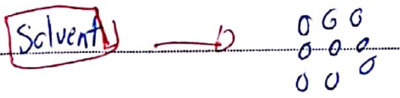
How Solutes dissolve in solvent.?

يتشتت

1- Solute bulk disperses into individual molecules

ΔH_1 = Positive.

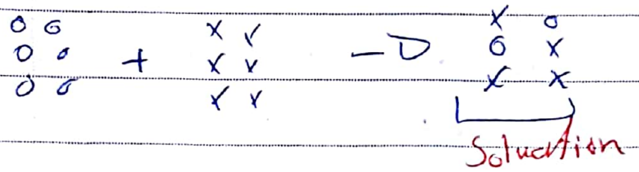
2- Solvent particals seperate from eachother



ΔH_2 = Positive.

3- mixing $\Delta H3 \rightarrow -\,,+$

يعتمد على المواد المتفاعلة.



يحصلون في نفس الوقت

التغير فيزيائي

ΔH = positive intermolecular تكسير روابط

$\Delta H_{Soluation} = \Delta H_1 + \Delta H_2 + \Delta H_3$

* what determines the sign of ΔH_{sol} * is only $\Delta H3$

* if ΔH_{sol} is negative, it is most likely the solute will dissolve in the solvent

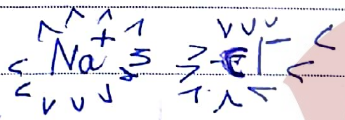
* if ΔH_{sol} is positive the solute will most likely will not dissolve.

* two Factores offecting the Solubility.

1- energy ($\Delta H_{solvation}$)

2- tendency toward disorder (entropy)
تميل الفوضى

$Na^+ \; Cl^- + H_2O \rightarrow$



(اقل فوضى) تم ترتيبهم

No.

لا يمكن الوصول الى درجة سالبة.

$\Delta G = \Delta H - T\Delta S$

Gibbs energy — enthalpy of Solution — entropy

ΔS + موجب فوضى اكثر. (−) فوضى اقل

(−) → يكون تلقائي.
(+) → لا يتم.

✓	−	−	+
*	+	+	−
حسب الظروف.		−	−
،،	،،	+	+

Nacl dissolves in water

Agcl doesn't dissolve → because of entropy.

Solubility Rule: like dissolve like.

Soluate. الشبيه يذوب الشبيه

* ionic and polar compound dissolve in polar Solvent.
* non polar Soluate dissolve in non-Polar Solvents.

في الأغلب صحيح ولكن يوجد استثناءات.

examples

ionic in Polar Nacl in Water

polar in Polar glucose in water.

non-Polar in Non-Polar ccl4 in benzene.

ccl4 in water لا يذوب
non-Polar Polar

3- no effect by tem   changes by temp   no effect by temp.

Example. Find the molality of a 2.45 M Solution (methanol in water) (d solu = 0.976 g/mL)

aqeous => محلول مائي
يعني اعتبره ماء

Solution :-

? $m = \frac{mole}{Kg\ OF\ solvent}$, √ $M = \frac{mole}{Litter\ of\ Solution}$

assum that you have. 1 L Solution.

moles of Solute $= 2.45 \frac{mol}{L} \times L = 2.45\ mol$

mass of Solute. $= 2.45\ mole \times 32.02 \frac{g}{mole} = 78.4\ g$

mass of Solution $= 1000 mL \times 0.97 \frac{g}{mL} = 976\ g$

mass of Solvent $= 0.976 Kg - 0.0784 Kg = 0.898 Kg.$

$m = \frac{2.45}{0.898} = 2.73 m$

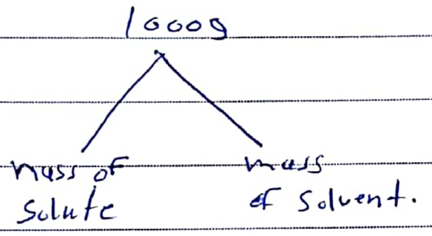
No.

example. Convert 35.4% to molality H_3PO_4 Solution ($M.m = 97.99 \frac{g}{moll}$)

Solulation.

$\text{mass \%} = \frac{\text{mass of Solute}}{\text{mass of soluation}}$, $m = \frac{\text{mole of solute}}{\text{mass of Solvent}}$.

assum you have 1kg of Solution.



$\text{mass of Solute} = \frac{35.4}{100} \times 1000 = 354 \text{ g}$

646 g =

$\text{mass of Solvent} = 1000 - 354 = 646 \text{ g}$ = 0.646 kg

$\text{moles of Solute} = \frac{354}{97.99} = 3.61$ mole.

$m = \frac{3.61}{0.646} = 5.59 \text{ m}$

No.

Effect of temp on Solubility.

* Solubility ⇒ max amount of solute that can be dissolved in certain amount of solvent to reach saturation at specific temp

* If the solute is solid ⇒ most of solid's solute, solubility increases by temp. يوجد شواذ

example. NaCl solubility increase by temp.

$Ce_2(SO_4)_3$ 〃 decreases by temp. ⇒ شاذة مثال عن

Note ⇒ No relation between ΔH solution with temp. to change the solubility.

ΔH sol ($CaCl_2$) = ⊖
ΔH sol (NH_4NO_3) = ⊕
} For both salts solubility increases by temp.

* If the solute is gas

For all gases (as solute), solubility decreas by temp

تزداد السرعة (الطاقة الحركية) بزدياد الدرجة فتزيد فرصة هروب جزيئات الغاز من المحلول وعدم ذوبانها.

by increasing the temp. KE of the gas particale increase ⇒ faster the particals ⇒ more chance to escape from the solution.

Effect of pressure on Solubility.

* If the Soild and liqud is the solute, changing the pressure does not offect the solubilty.

* If the Solute is gas, then Solubility increasing by increasing the pressure.

- according to the KMT increasing the pressure → more collisions of the gas with the surface of the liquid → increase on the probability of capturing the gas particles

$C \propto P$

$C = KP$

(Henry's law)

C → Connecentration of gas in the Solvation.

P → pressure of the gass

K → proportinality Constant.

(Henry's constant)

كل غاز له ثابت مختلف

بتغير درجة الحرارة يتغير K وبالتالي

تتغير الذائبية

No.

example. ⇒ If the Solubility of Pure N_2 (g) in water at 25C° and 1 atm is 6.8×10^{-4} mole/L what will be the conc of atmospheric N_2 in in water at the same conditions.

Pair 1atm

$\to P_{N_2} = 1atm \times 0.76$

$\to PO_2 = 1atm \times 0.21$

$C = pk$

$C = 6.8 \times 10^{-4} \times 0.78$

$C = 5.3 \times 10^{-4}$ M

$K = \frac{c}{P} = \frac{6.8 \times 10^{-4}}{1}$

* Note.

* Solubility of gases increases by increasing the Pressure.

* Solubility of gass decreas by increasing temp

* Solubility of gas increasies if there is a reaction between the gas and the Solvent.

$CO_2(g) + H_2O(L) \to H_2CO_3(aq)$

$HCl(g) + H_2O(L) \to HCl(aq)$

$NH_3(g) + H_2O(L) \to NH_4OH(aq)$

O_2 in water
O_2 in blood → الذائبة أكثر لأن الأكسجين
يتفاعل مع هموغلبين

Collegative properties of soluation.
→ properties that depends only on the amount of Solute in the Soluation.

1- vapor pressure lowering
2- boiling point elevation.
3- freezing point depression.
4- osomotic pressure.

We compair properties of pure Solvent with soluation.

① If the Solute is none volatile → the V.P of its Soluation is always less than that of the pure Solvent.

Raoult's law

$P_1 = X_1 \; P_1^{\circ} \rightarrow$ pure → P_1 : V.P of the Solution
P_1° : V.P of pure Solvent

X_1 = mole fraction

$$\rightarrow X_1 = \frac{\text{moles of Solvent}}{\text{moles of Solute} + \text{moles of Solvent}}$$

X_1 takes the values from $\boxed{0 \text{ to } 1}$

No.

X_2 = mole fraction of the solute

$$X_1 + X_2 = 1$$

$$\boxed{X_1 = 1 - X_2}$$

$$P_1 (1 - X_2) P_1^\circ$$

$$P_1 = P_1^\circ - P_1^\circ X_2$$

$$P_1^\circ - P_1 = X_2 P_1^\circ$$

$$\boxed{\Delta P = X_2 P_1^\circ}$$

* ΔP is directly proportional to ⇒ the concentration (measured in mole fraction) of the solute present.

$P_1^\circ = 0.78$ atm

$\Delta P = +0.12$ atm

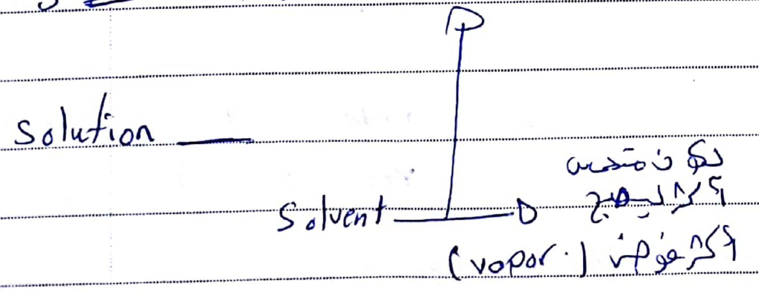
$P_1 = ??$

$0.78 - 0.12 = 0.66$ atm

lowering. [illegible]

entropy (solution) larger than (pure solvent) كل شي بيصير ، ليصبح الفوضى.

S = vapor



No.

1. ⓑ If the Solute is volatile. (ethanol in water)

- $V.P_{Solute} = X_{Solute} \overset{pure}{P^o_{Solute}}$.

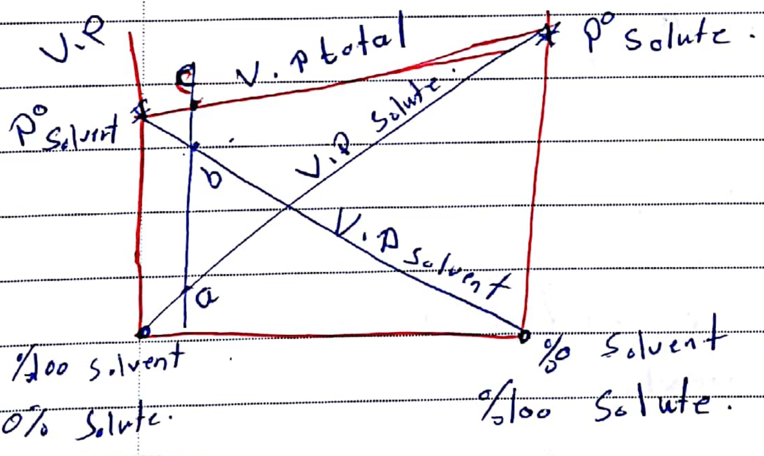
- $V.P_{Solvent} = X_{Solvent} P^o_{Solvent}$.

$V.P_{total} = V.P_{Solute} + V.P_{Solvent}$

$V.P_{total} = X_{solute} P^o_{Solute} + X_{Solvent} P^o_{Solvent}$.

$= X_{solute} P^o_{Solute} + (1 - X_{Solute}) P^o_{Solvent}$.

!! remember ⇒ $X_{Solute} + X_{Solvent} = 1$



you can do it

$\boxed{c = a + b}$

① Solute is Volatile.

② the Solution is ideal (which obays Roault's law) يطيع

ومعناه (ΔH_{sol} = zero)

(Solute and Solvent particles are similar)

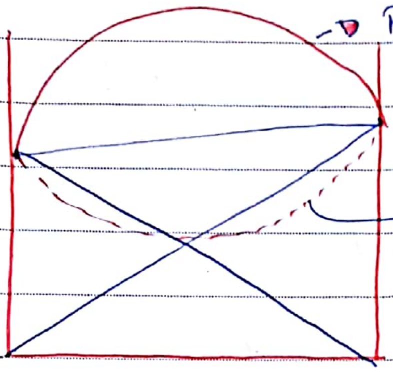
▶ The intermolecular forces between Solute and Solvent molecules are equal to those between solute molecules and between Solvent molecules

cyclohexane.

in

benzene.

No.



- Positive deviation
  لا ينجذبون بعض فيميلوا للخروج
  والانفصال بعض فتزيد الضغط

ΔH_{solu} موجب

- negative deviation
  لو ينجذبون لبعض فيقل الضغط
  فيصعب عن بعض ويكونوا [illegible]
  (بخار ينقص)

ΔH_{solu} سالب

② Boiling point elevation

- Boiling point of Solution is higher than that of of the pure Solvent.

$$\underbrace{\Delta T_b}_{\text{increase in the B.p}} = \underbrace{K_B}_{\text{constant depends on the Solvent.}} \; m \rightarrow \text{molility.}$$

③ freezing point depression

- Freezing point of a Solution is lower than that of Pure Solvent.

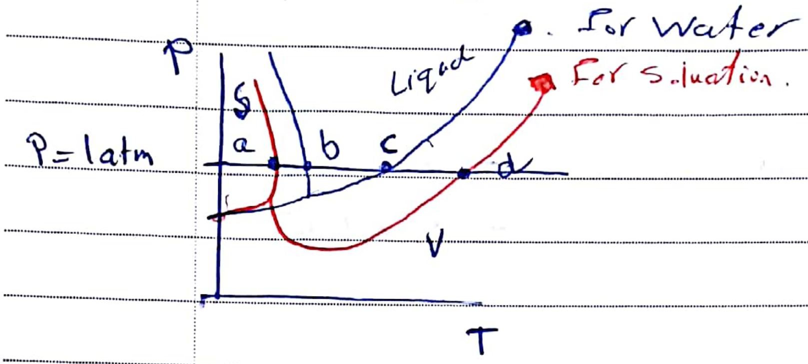
$$\underbrace{\Delta T_f}_{\text{freezing point depression}} = K_f \; m$$

* $K_f \neq K_b$

لكن
في الحالتين يكون موجب بالأولى دائماً تزيد
والثانية نطرح.

No.

* phase digram



a => fussion the Solution
b => " " Solvent
c => vaporization of Solvent.
d => " " Soluation.

example.

ethylene glycol $CH_2 - CH_2$ => non-volitale
$\quad\quad\quad\quad\quad\quad\quad | \quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad OH \quad\quad OH$

651g E.G dissolved in 2505g water. what is the freezing point of the solution, given that

M.m = 62.0 g/mol

$K_f(H_2O) = 1.86$ c/m , $K_b = 0.52$°c/m

B.P(E.G) = 127°c.

Solution

$\Delta T_f = k_f \ m$

$$m = \frac{\text{moles of Solute}}{\text{mass Solvent}}$$

$$\text{moles} = \frac{651}{62.0} = 10.5 \Big/ \frac{\text{moles}}{\text{mass in kg}} = \frac{10.5}{2.505} = 4.19$$

$\Delta T_f = K_f\, m$ ⇒ مقدار النقصان في الدرجة

$= 7.79\ C^\circ$

F.P of the solution = 0 - 7.79°C.

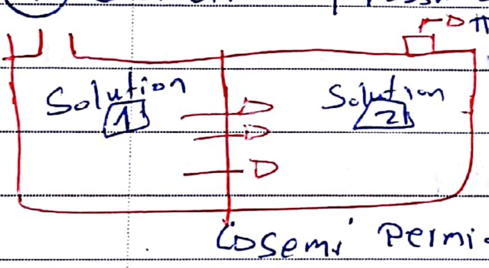
= - 7.79°C

$\Delta T_b = K_b\, m$

$= 0.52 \times 4.29 = 2.2$

B.P of the solution = $\underset{\text{درجة غليان الماء}}{\underline{100}} + 2.2 = 102.2\ C^\circ$

④ Osmotic pressure.



[Solution2] > [Solution1]

* if [Solution 2] = [Solution 1] ⇒ ΔG = Zero.

$\pi = MRT$

- units of π $= \dfrac{\cancel{mole}}{\cancel{L}} \times \dfrac{\cancel{L}.atm}{\cancel{mole}.\cancel{K}}\ .\cancel{K} = atm$ 0.0821

If the two solution have the same molarity ⇒ isotonic solution

For different con.. solutions with higer conc,

// " with lower ~~t~~ hypertoric.

Solution will higher conc hypertoric

455
458
456

For different con. Solutions with higer conc.
// // width lower ~~hypertoric~~ hypotonic
Solution with higher conc hypertoric

* asmosis ⇒ The net movement of solvent molecules 455
through a semipermeable membrane from a pure Solvent 458
or dilute Solution to amore concentrated 456
solution.

x asmotic pressure :- the pressure required to stop asmosis

example.

7.85 g of of a compound was dissolved in 301g of benzen, the freezing decreased by 1.05C°, what is the M.M of the compound. ((Kf-(benzen)) = 5.21g/mol

Solution:-

$\Delta T_f = K_f\, m$

$1.05 = 5.21 \times \frac{7.85}{0.301 \cdot MM}$

M.M = 127g/mol.

35 g of Hb where dissolved in water to make 1.00L Solution, the measred O.P was 10. torr(mmHg) at 25 °C. cal the M.M of Hb

~~$\pi = kRt$~~ $\pi = RTM$

No.

$\pi = MRT$

$10 \frac{\cancel{torr}}{mmHg} \times \frac{1 atm}{760 \cancel{mmHg}} = 0.013 atm$

$0.013 = \frac{350}{1L \cdot M.M} \times 0.0821 \times 298 = 65079 g/mol$
$= 6.5 \times 10^4$

· ucl 500 →

* If M.M ≥ 500 g/mol ⇒ use osomtic pressure
* If M.M < 500 g/mol ⇒ use F.P depression.

So for the Solute is assumed as a non-assocIating non dissociting solute. in the Solution

$1\ glucose_{(s)} \xrightarrow{H_2O} 1\ glucose_{(aq)}$

$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$ dissocicting

$MgCl_{2(s)} \xrightarrow{H_2O} Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$

No.

- $\Delta T = K m$ m, M for particles not for solute molecule.
- $\Pi = MRT$

$\Delta T_f = iK_f m$ i = van't Hoff Factor

$\Delta T_b = i K_b m$

$\Pi = iMRT$

$CH_3COOH_{(l)} \xrightarrow{H_2O} CH_3COOH_{(aq)}$ i = 1.2

تفككه جزئي لأنه حمض ضعيف.

chapter $\boxed{14}$ chemical kintics

→ rate of chemical rxn / rxn rate.

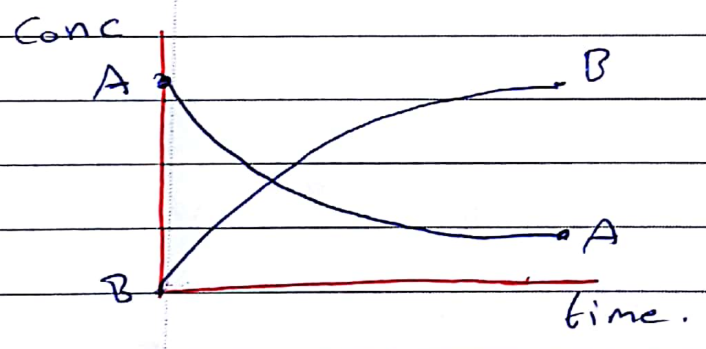
rate ⇒ change in conn by time ⇒ $\frac{M}{s}$

* $A \rightarrow B$

rate of rxn = rate dissappearnce. of A

" appearence of B.

$$= \frac{-[A]}{\Delta t} = \frac{[B]}{\Delta t}$$



* $A \rightarrow 2B$

$$\text{rate} = \frac{-2d[A]}{dt} = \frac{d[B]}{dt}$$

$$= \frac{-d[A]}{dt} =$$

No.

* $aA + bB \rightarrow cC + dD$

→ rate $= -\frac{1}{a}\frac{d[A]}{dt} = 1 \cdot \frac{d[A]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

* rate expression

example. Write the rate expression

* $I^-_{(aq)} + OCl^-_{(aq)} \rightarrow Cl^-_{(aq)} + OI^-_{(aq)}$

Solution →

$$-\frac{d[I^-]}{dt} = -\frac{d[OCl^-]}{dt} = \frac{d[OI^-]}{dt}$$

* $3O_{2(g)} \rightarrow 2O_{3(g)}$

$$-\frac{1}{3}\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[O_3]}{dt}$$

* $4NO_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$

$$\frac{1}{4}\frac{-d[NO_2]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[N_2O_5]}{dt}$$

- If the rate of dissapearance of $O_2 = 0.024$ M/s what is the rate of dissaperance of NO_2

$$\frac{-d[O_2]}{dt} = \frac{-d[NO_2]}{4\,dt} \Rightarrow 4 \cdot 0.024 = 0.096 \text{ m/s}$$

* يا نكتب اشارة السالب او نكتب
rate of dissapeance للتعبير عن النقصان

No.

Rate lows.

expermentally the rate of rxn depends on the conc. of reactants only.

$A + B \rightarrow C + d.$

rate $\propto [A][B]$

rate $= K[A]^{a}[B]^{b}$ → rate low

K: rate constant.

a: order with recpact A

b: " " " B

a+b: overalle order.

a, b: integer

→ No relation between orders the stoichiometric amounts of the reactants.

units → $\frac{M}{s} : K M^{a} M^{b}$

$\frac{M}{s} : K M^{a+b}$

$\frac{M}{s} : \boxed{K} M^{\text{overall order}}$

→ units of K depends on the overall order.

0th order rxn أنواع التفاعلات حسب الرتب

1st order rxn

2nd order rxn

Zeroth order rxn. A + B → C + D

rate = $k[A]^0[B]^0$ overall order = 0 + 0 = 0

rate = k } → [illegible]

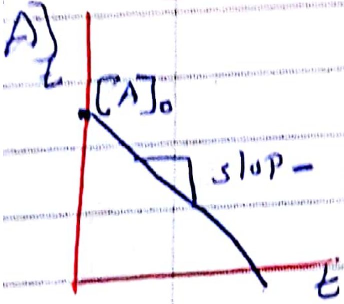
$$\frac{-d[A]}{dt} = k$$

$$\int_{[A]_0}^{[A]_t} d[A] = \int_0^t -k\,dt$$

[illegible]

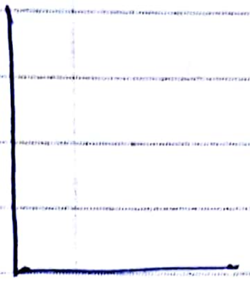
$$[A]_t - [A]_0 = -k(t - 0)$$

$$[A]_t = [A]_0 - kt$$ integrated rate law for the zeroth order rxn.



* الحالة الوحيدة الي فيها تركيز
المادة المتفاعلة بتخلص وبيصير الـ (0th
عندما يكون (0th = overall)

example. For 0th order rxn at what time the reactants will be completly consumed.



* $[A]_t = [A]_0 - Kt$

$0 = [A]_0 - Kt$

$t = \frac{[A]_0}{K}$

*

half life time

time required to reach half the inital conn.c

$$\frac{[A]_0}{2} = [A]_0 - Kt$$

$$\boxed{t_{\frac{1}{2}} = \frac{[A]_0}{2K}}$$

half life time

1st order rxn $A \rightarrow B$

rate law

$\Rightarrow$ rate $= K[A]^1$

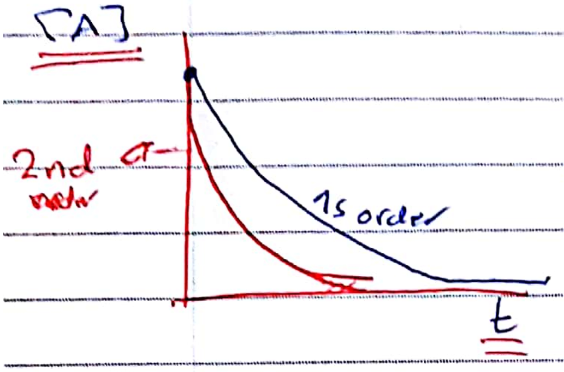
$$\frac{-d[A]}{dt} = K[A]$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -K\int_0^t dt$$

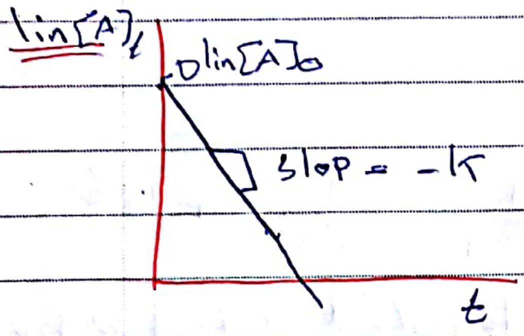
$$\text{lin}[A]_t - \text{lin}[A]_0 = -kt$$

No.

$\ln[A]_t = \ln[A]_0 - kt$ → integrated rate law for the 1st order rxn.



في حالة نقصان باستمرار
ولكن لا تصبح التراكيز
ولا يتوقف التفاعل
إلا لوقت ∞



half life time.

$\ln\frac{[A]_0}{2} = \ln[A]_0 - kt$

$\ln[A]_0 - \ln 2 = \ln[A]_0 - kt$

$t_{\frac{1}{2}} = \frac{\ln 2}{k}$

unit for k

rate = k[A

$\frac{M}{s} = k\,\cancel{M}$

$k = \frac{1}{s}, s^{-1}, Hz$

2nd order rxns $A + B \rightarrow C$

rate = $k[A]^2[B]^0$

rate = $k[A]^1[B]^1$ × "سطحي"

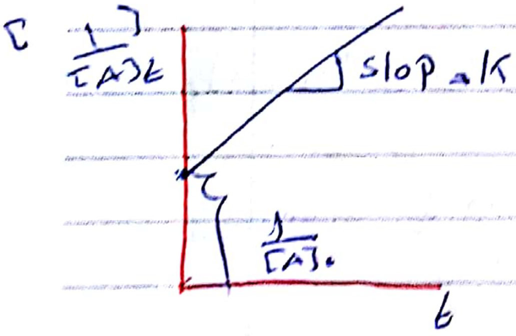
$$\frac{-d[A]}{dt} = k[A]^2$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\int \frac{1}{x^2}\,dx = \frac{-1}{x}$$

$$\Rightarrow \frac{1}{[A]_0} - \frac{1}{[A]_t} = -kt \Rightarrow \boxed{\frac{1}{[A]_t} = \frac{1}{[A]_0} + k \cdot t}$$

integrated rate law for 2nd order r/n.



half life time.

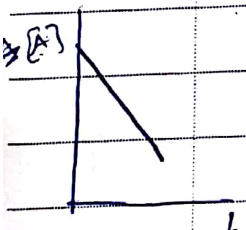
$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt$$

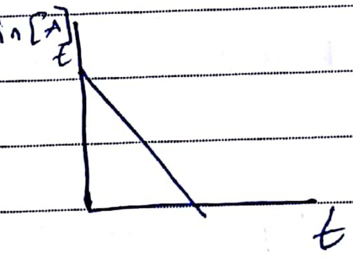
$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt \Rightarrow t_{\frac{1}{2}} = \frac{1}{[A]_0 k}$$

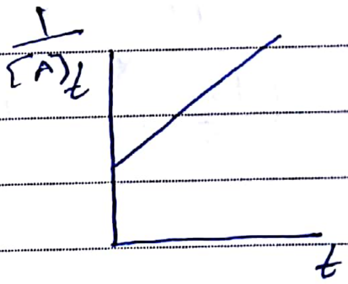
unite For $K \Rightarrow \frac{M}{sec} = K M^2$

$$K = \frac{1}{sec.M}$$

0th	1st	2nd.
$rate = K$	$rate = K[A]$	$rate = [A]^2 K$
$[A]_t = [A]_0 - Kt$	$lin[A]_t = lin[A]_0 - Kt$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + Kt$
$\frac{M}{S}$	$\frac{1}{S}$	$\frac{1}{M.S}$
$_{\frac{1}{2}}t = \frac{[A]_0}{2K}$	$t_{\frac{1}{2}} = \frac{lin2}{K}$	$t_{\frac{1}{2}} = \frac{1}{[A]_0 K}$







* How to determine the order.

$aA + bB \rightarrow$ Products.

$rate = K[A]^x[B]^y$

to find (x) and (y) do experiment.

example.

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$rate = k[NO]^x[H_2]^y.$$

exp	$[NO]$	$[H_2]$	Initial rate	
1	5×10^{-3} M	2.0×10^{-3} M	1.3×10^{-5} M/s.	$x = 2$
2	10×10^{-3} M	2.0×10^{-3} M	5×10^{-5}	
3	10×10^{-3}	4.0×10^{-3}	10.0×10^{-5}	$y = 1$

[illegible]

$$\frac{rate(1) = 1.3\times10^{-5} = \boxed{k}(5.0\times10^{-3})^x(2.0\times10^{-3})^y}{rate2 = 5\times10^{-5} = k(10.0\times10^{-3})^x(2.0\times10^{-3})^y.}$$

$$\frac{1.3}{5} = \left(\frac{5}{10}\right)^x.$$

$$\frac{5}{1.3} = \left(\frac{10}{5}\right)^x \Rightarrow 4 = (2)^x \quad \therefore \boxed{x = 2}$$

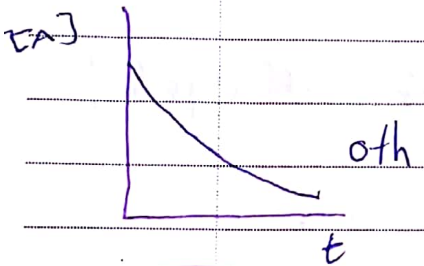
$$\frac{rate_2}{rate_2} = \left(\frac{10}{5}\right) = \frac{\cancel{k}}{\cancel{k}}\frac{\cancel{(10\times10^{-3})^2}(4\times10^{-3})^y}{\cancel{(10\times10^{-3})^2}(2\times10^{-3})^y}.$$

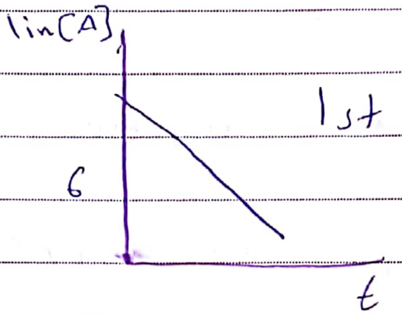
$$2 = (2)^y$$

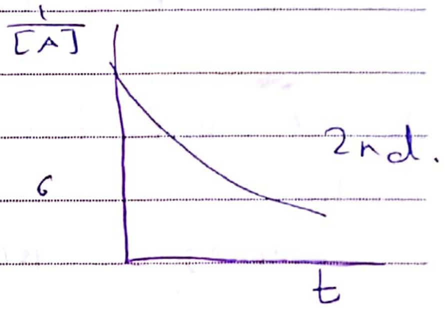
$$\boxed{y = 1}$$

$A + B \longrightarrow$ Product.

time	conn	ln[ ]	$\frac{1}{[\ ]}$
0	$[A]_0$		

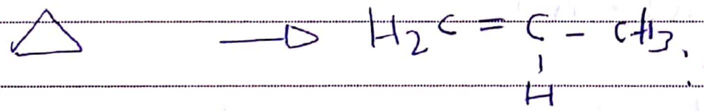






example.

cyclopropane $\longrightarrow$ 1- propene.



$$\triangle \longrightarrow H_2C = \underset{H}{\overset{}{C}} - CH_3.$$

1st order rxn
موجودة كامكن تحريرالزتية.
$k = 6.7 \times 10^{-4}$ s^{-}

a) what is the conc at cyclo after 8.8 min
if $[cyclo]_0 = 0.25M$

$\ln[A]_t = \ln[A]_0 - kt$

$\ln[A]_t = \ln(0.25) - 6.7 \times 10^{-4} \times (8.8 \cdot 60)$

$\ln[A]_t = -1.74$,

$[A]\ e^{-1.74} = 0.18\ M$

No. تتمة الدرس

b) How much time it takes to have $[A]_t = 0.15\,M$

$\ln[A]_t = \ln[A]_0 - kt$

$\ln[0.15] = \ln[0.25] - 6.7\times10^{-4}\,t$

$t = 7.6\times10^{2}\ \underline{\underline{s}}$

c) How much it takes to consume 74% of cyclo?

Solution :-

remaining of cyclo = 100% − 74% = 26%

$[\text{cyclo}] = 0.25\times0.26 = 0.065\ M \rightarrow$ [illegible] $\times$

$\ln[A]_t = \ln[A]_0 - k\underline{\underline{t}}$

$\ln[0.065] = \ln[0.25] - 6.7\times10^{-4}\,t$

$t = 2.0\times10^{3}\ s$

No.

Activation energy and temp dependance.

chemical reaction : particle collisions.

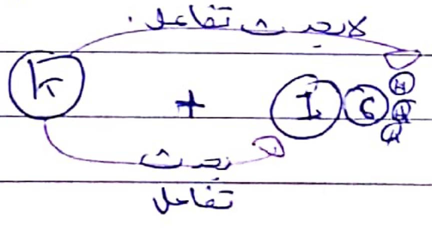
K.E for particles ∝ temp.

as temp increase → K.E increase. → Speed increase.

faster the rxn ← collisions increase. ←

* Not all collisions lead to products.
* minimum amount of energy must be over come ⇒ c called activation energy (Ea)

* $K + ICH_3 \rightarrow KI + CH_3$.



frequency factor (A)

* Arrheneous equation :

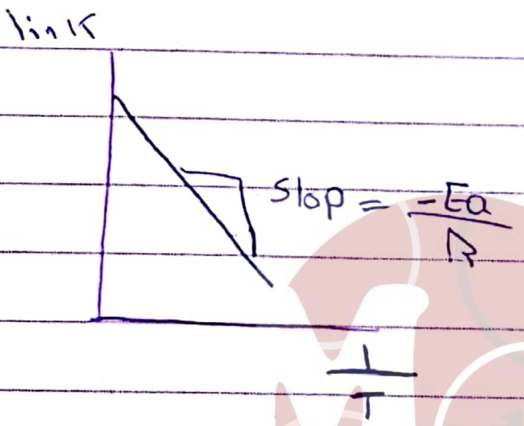
$$K = Ae^{-\frac{Ea}{RT}}$$

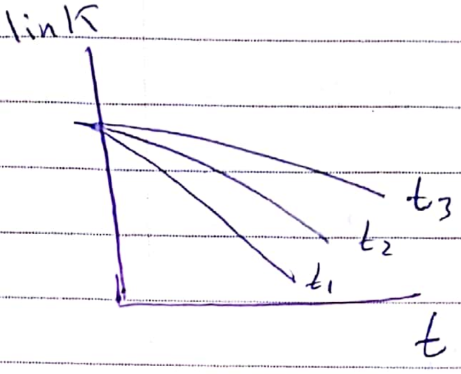
عكسي

طردي

طردي

$$\underbrace{\text{lin } K}_{y} = \underbrace{\text{lin } A}_{a} - \text{lin } \underbrace{\frac{Ea}{RT}}_{b}$$





$T_1 > T_2 > T_3$ (slop)

* Ea and A are positive number.

* at ~~does~~ two different temps.

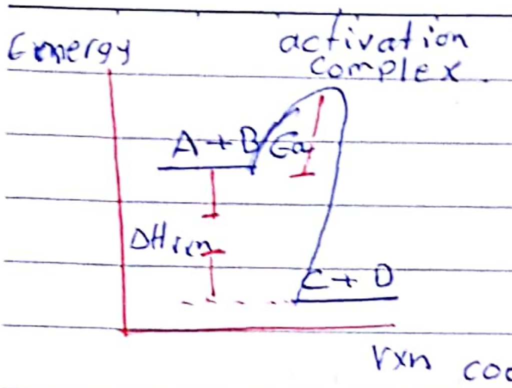
$$\text{lin}\,\underline{\underline{K_1}} = \text{lin}\,A - \frac{Ea}{R\underline{\underline{t_1}}} \quad \text{at } t_1$$

$$\text{lin}\,\underline{\underline{K_2}} = \text{lin}\,A - \frac{Ea}{R\underline{T_2}} \quad \text{at temp } T_2$$

$$\text{lin}\,K_1 - \text{lin}\,K_2 = \frac{-Ea}{RT_1} + \frac{Ea}{RT_2}$$

$$\text{lin}\,\frac{K_1}{K_2} = -\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

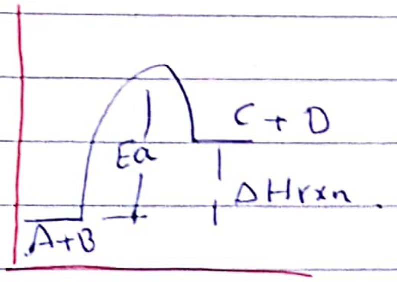
No.



$$A + B \rightarrow C + D$$

* For backwed rxn

$$Ea_{back} = Ea_{forward} - \Delta H_{rxn}$$



Exothermic.

*

تزداد طاقة التنشيط تقل سرعة التفاعل فالتفاعل الأول هو الأسرع.

example.

For a first order reaction, $k = 3.46\times10^{-2}\ s^{-}$ at 25 °C

$Ea = 50.2\ kJ/mol$

what is the rate constant (k) at 77 °C ?

Solution :-

$$\ln \frac{3.46\times10^{-2}}{k_2} = \frac{-50.2\times10^{3}}{8.314}\left(\frac{1}{298} - \frac{1}{350}\right)$$

$$\frac{3.46\times10^{-2}}{k_2} = e^{-3.01} \Rightarrow k_2 = 0.702\ s^{-}$$

No.

* Reaction mechanism.

overall rxn ($A \rightarrow B$)

mechanism $A \rightarrow C$ → elementary step 1

$C \rightarrow 2E$ → " " 2

$E \rightarrow M$ → " " 3

$M \rightarrow E \rightarrow B$ → " " 4

No.

14.5

* Reaction mechanism.

overall rxn $(A \rightarrow B)$

mechanism $A \rightarrow \cancel{C}$ → elementary step 1

$\cancel{C} \rightarrow 2\cancel{E}$ → " " 2

$2\cancel{E} \rightarrow \cancel{M}$ → " " 3

$\cancel{M} + \cancel{E} \rightarrow B$ → " " 4

في النهاية $\boxed{A \rightarrow B}$

مراجعة

18 g of non-volitc paraffin (molar mass = 282g/mol) was dissolved in 500 g of benzene (M.mass 78. At 53° (the vapor pressure of benzen is 300.0 mmHg what is the V.p lowering (in mmHg) for the solution of this temp ?

$\Delta P = X_2 P_1^\circ$

$X_2 = \dfrac{\text{moles of solute}}{\text{total moles}}$

$= \dfrac{18.0/282}{(18/282) + 500/78}$

A 0.100 m K_2SO_4 aquous solution has : freezing point of -0.43 C°. what is the van't Hoff factor for this solution.

No.

$\Delta T_f = i K_f m$

$0.43 = i\,(1.8)(0.1)$

For a correct mechanism :-

شرطين اذا تحققوا بنحكي It could be mechanism

* The Sum of all rxn mechanism steps (elementary step) must give the over all rxn (must give the overall blanced equation) ,

* The rate of over all rxn is controled by the " rate determing step" ; which is the slowest step in the mechanism.

$2NO + O_2 \longrightarrow 2NO_2$ rate $= K[NO]^x[O_2]^y$

mechanism

$2NO \longrightarrow N_2O_2$ rate $= K_1[NO]^2$

$N_2O_2 + O_2 \longrightarrow 2NO_2$ rate $= K_2[N_2O_2]^1[O_2]^1$

N_2O_2 intermediate molecules (متوسط)

rxn molecularity → فقط تصف (elementary step)

over all rxn.

- (unimolecular elementary step with one reactant)
- bimolecular ثنائي الجزيء.
- Termolecular extremely ra

→ is the number of molecules reacting in an elementary step

$I^- + 2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + I^-$ $\boxed{2nd\ order}$

* experimentally rate $= k[H_2O_2][I^-]$

* mechanism

$H_2O_2 + I^- \rightarrow H_2O + IO^-$

$H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

IO^- : intermediate I^- : catalysit

$\rightarrow$ rate $= k_1[H_2O_2]^1[I^-]^1$

$\rightarrow$ rate $= k_2[H_2O_2][IO^-]$

ال (elementeray step) بـ order تعيين الخطوة الي بتحدد السرعة

for a rxn, the rate low:

rate $= k[NO_2]^2$

mechanism:

$\cancel{NO_2} + NO_2 \rightarrow NO + \cancel{NO_3}$ rate $= k_1[NO_2]^2$ slowest

$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$ rate $= k_2[NO_3]^1[CO]^1$

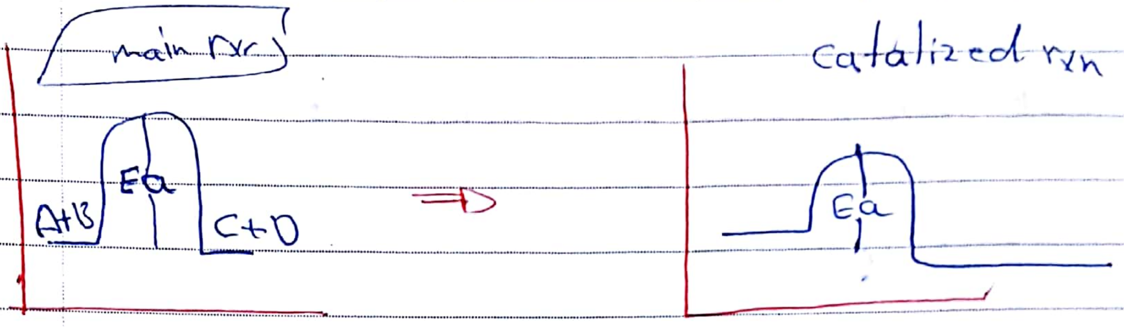
over all rxn: $NO_2 + CO_2 \rightarrow CO_2 + NO$

intermdate: NO_3 NO_2

intermedate ما بكون موجود بـ (over all rxn)

Catalyst: Substance added to the rxn to increase it's speed by opening another rxn pathway with lower activation energy

$\boxed{\text{speed, Ea}}$ علاقة عكسية بين



rate of catalized rxn > rate uncatalized rxn

K catalized > K uncatalized.

Ea catalized < Ea uncatalized.

Types of catalyst

1- Heteogeneous: Catalyst and reactants in different phases

* Example. - Synthesis of NH_3

$2N_2 + 3H_2 \rightarrow 2NH_3$

catalyst ($Fe + K$, Al_2O_3)

- manufacturing of HNO_3

$4NH_3$

No.

Catalytic converter contains Pt (بلاتين), Pd (بلاديوم) ، CuO , Cr_2O_3.

NOx , CO (مواد سامة.)

$2NO \rightarrow N_2 + O_2$

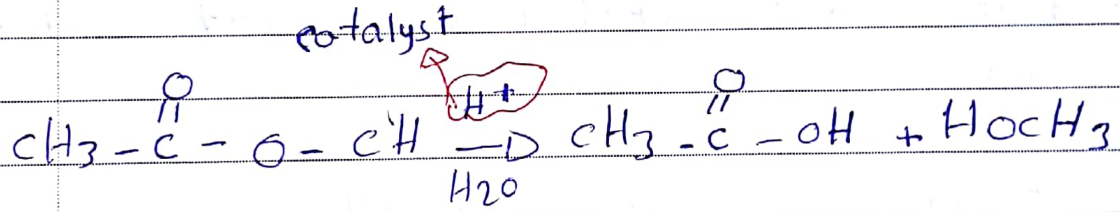
$2NO_2 \rightarrow N_2 + 2O_2$

$2CO + O_2 \rightarrow 2CO_2$

النواتج أقل سمومية

② Homogenous catalysis

catalyst is with the same phase of the reactants



$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH \xrightarrow[H_2O]{\overset{\text{catalyst}}{H^+}} CH_3-\overset{\overset{O}{\|}}{C}-OH + HOCH_3$$

③ enzymes

- * catalyst for biological rxns.
- * catalize very specific rxns.
- * Speeds up biological rxns from 10^6 to 10^{18} times.

$S + E \rightleftharpoons ES$

S "Sapstrate"

$ES \rightarrow E + \text{product}$ R.D.S

No.

"Chapter 15" chemical equilibrum.

$A + B \rightarrow C + D$

once $\boxed{C}$ and $\boxed{D}$ exist they react to Form A and B

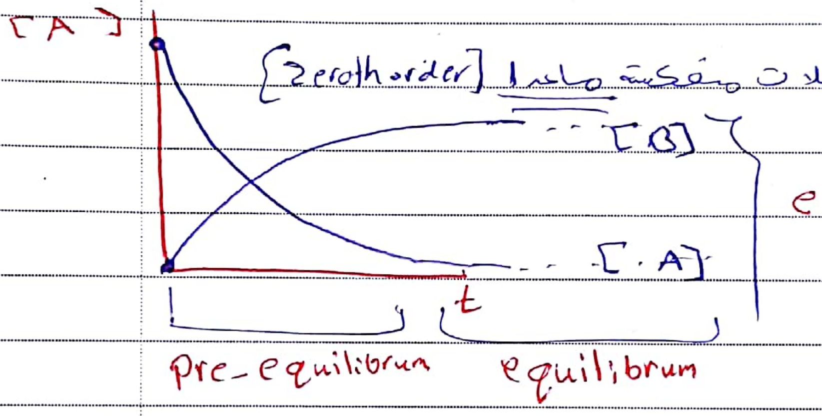
$C + D \rightarrow A + B$

$\rightarrow$ $A + B \rightleftarrows C + D$

تفاعلات عكسية

[zerothorder] كالتفاعلات منعكسة تماما * reversible rxns

$A \rightleftarrows B$



* when constrution of reactiant and products don't change $\rightarrow$ the system is said to be in equilitrum.

* because rate of production of products equals the rate disspearnce of the products.

$\rightarrow$ $N_2O_4(g) \rightleftarrows 2NO_2$ (chemical equlibrum)

$\rightarrow$ $H_2O(l) \rightleftarrows H_2O(s)$ (physical equlibrum)

* Experimentally it was found that

the ratio of product of product conc. to the product of reactants conc. is constant.

$$\Rightarrow \text{constant} = \frac{\overset{\text{مضروب}}{\Pi}\,[\text{product}]}{\Pi\,[\text{reactants}]} = K$$

K ⇒ equlibrium constant.

$\Rightarrow$ $A \rightleftharpoons B$

$$K = \frac{[B]}{[A]}$$

* $2A \rightleftharpoons B$ $\quad K = \frac{[B]}{[A]^2}$

* $aA + bB \rightleftharpoons cC + dD.$ $\quad K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

* $N_2O_4 \rightleftharpoons 2NO_2$ $\quad K = \frac{[NO_2]^2}{[N_2O_4]}$

* because rate constant are temp. dependent, it follows that the equilibrum constant must also change with temp.

No.

* $A + 2B \underset{K_1}{\overset{K_2}{\rightleftharpoons}} AB_2$

- rate 1 = $K_1 [A]^1 [B]^2$

- rate 2 = $K_2 [AB_2]$

~> at equilibrum rate 1 = rate 2

$$K_1 [A]^1 [B]^2 = K_2 [AB_2]$$

$$\frac{K_1}{K_2} = \underbrace{\frac{[AB_2]}{[A][B]^2}}$$

rate constant. $\leftarrow \frac{K_1}{K_2}$ = K (equlibirum constant)

* if K >> 1 rxn mixture is mainly made from products.

* if K << 1 rxn mixture is mainly made from reactants.

$CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$

$K_a = 1.8 \times 10^{-5}$.

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

units of K

$\boxed{K}$ is unitless always.

No.

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $\Rightarrow K_c = 10^{-10}$

[illegible]

* $N_2O_4 \rightleftharpoons 2NO_2$

$$K = \frac{[NO_2]^2}{[N_2O_2]}$$

$K =$ $aA + bB \rightarrow cC$

$$K = \frac{[C]^c}{[B]^b[A]^a}$$

$$\underline{\text{true } K} = \frac{a_C^c}{a_A^a \; a_B^b}$$

a: activity.

$$a = \frac{[\text{Conc.}]}{\text{Conc. unite.}}$$

---

what is $[H_2O]$

$$M = \frac{\text{mol.}}{\text{volume}}$$

assume that you have 1L water

1000g

$\downarrow$

$$\frac{1000\,g}{18\ g/mol}$$

$= 55.6$ mol

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K' = \frac{[H_3O^+]_{aq}[CH_3COO^-]_{aq}}{\underbrace{[H_2O]}_{\text{constan}}[CH_3COOH]}$$

$$\Rightarrow K_a = \frac{\underbrace{[H_3O^+]}_{\text{or } [H^+]}[CH_3COO^-]}{[CH_3COOH]}$$

* types of "K"

- Kc : equilib contant in terms of conc.
- Kp : " " of partial pressure.
- Ka : " = = = of conncentration of acid.

Kb : " = = = " of basis

$K_w = K_a . K_b = 10 \times 10^{-14}$ → constant.

calculs

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_2]} \quad , \quad K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

$$aA_{(g)} \rightleftharpoons bB_{(g)}$$

$$PV = nRT$$

$$P_A V = n_A RT \Rightarrow P_A = \frac{n_A}{V} RT \Rightarrow P_A = [A]RT$$

$$P_B V = n_B RT$$

$$\Rightarrow P_B = \frac{n_B}{V} RT = P_B = [B]RT$$

$$K_p = \frac{P_B^b}{P_A^a} = \frac{([B]RT)^b}{([A]RT)^a} = \underbrace{\frac{[B]^b}{[A]^a}}_{K_c} . (RT)^{b-a}$$

$$\boxed{K_p = K_c (RT)^{\Delta n}}$$

$$\boxed{\Delta n = b - a}$$

No.

$K_p = K_c * (RT)^{2-1}$ ⇒ $K_p = K_c(\overset{0.0821}{R}T)$

$K_p \neq K_c$

⇒ $K_p = K_c$ only if $\underbrace{\Delta n = \text{zero}}$

moles of gases in the reactants equls moles of gase in the products.

example

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

if $K_p = 1.05$ and $(P_{PCl_5}) = 0.875$ atm

$(P_{PCl_3}) = 0.463$ atm

$(P_{Cl_2}) = ??$

Solution-

$$K_p = \frac{(P_{Cl_2})(P_{PCl_3})}{P_{PCl_5}}$$

$$1.05 = \frac{P_{Cl_2} \cdot 0.463}{0.875}$$

$(P_{Cl_2}) = 1.98$ atm.

⇒ if T = 25 C° calc. K_c

$K_p = K_c(RT)^{\Delta n}$

No.

$1.05 = K_c (0.0821 \times 298)^{2-1}$

$K_c = 0.0429$

example.

$$\underbrace{CaCO_3}_{}(s) \rightleftharpoons \underbrace{CaO}_{}(s) + CO_2\underbrace{(g)}_{}$$

⇒ hetrogenous equlibrum.

$$\underbrace{K_c}_{\text{constant}} = \frac{[CO_{2(g)}]\overbrace{[CaO_{(s)}]}^{\text{constant}}}{\underbrace{[CaCO_{3(s)}]}_{\text{constan}}}$$

تركيز الصلبة و السوائل ثابتة.

$K_c = [CO_{2(g)}]$

* $\frac{1}{2} N_2O_{4(g)} \rightleftharpoons NO_2(g) \Rightarrow K_{c_1} = \frac{[NO_2]}{\sqrt{[N_2O_4]}}$

$N_2O_{4(g)} \rightleftharpoons 2NO_2(g) \quad K_{c_2} = \frac{[NO_2]^2}{[N_2O_4]}$

$2NO_{2(g)} \rightleftharpoons N_2O_4(g) \quad K_{c_3} = \frac{[N_2O_4]}{[NO_2]^2}$

* $K_{c_2} = \frac{1}{K_{c_3}}$

* $K_{c_2} = (K_{c_1})^2$

For a neumerical (عددي.) value of equilib constant. A balanced chemical equaton must be givn.

(Kc + chemical eqaation + temp)

No.

What does K tell as :-

① $\frac{K_f \text{(الامامي)}}{K_b \text{(العكسي)}} =$ $K = 10^8$ $A \overset{\text{cl}}{\rightleftharpoons} B$ $K = 10^{-2}$ $C \overset{\text{cl}}{\rightleftharpoons} D$

② you can predict the direction of the rxn.

$H_2(g) + I_2(g) \rightleftharpoons 2HI$ $K_c = 54.3$ at 430 °C

If you mixed (0.243) mol of $H_2(g)$
(0.146) mol of $I_2(g)$
(1.98) mol of HI
mixed in 1L container.

$K_c = \frac{[HI]_e^2}{[H_2]_e [I_2]_e} = 5,4.3.$

e في حالة الاتزان

reaction quotiont $Q_c = \frac{[HI]_0^2}{[H_2]_0 [I_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$

0 في البداية

⇒ If $Q_c = K_c$ " في حالة اتزان "

If $Q_c > K_c$ rxn proceeds in the backward directi

If $Q_c < K_c$ " " " " forward.

اذا كانت احدى المواد المتفاعلة مفقودة (غير موجودة) سيكون backward (rxn)
ليعوض النقص في ظل العادة.

* $A + B \rightleftharpoons C + \underbrace{D}_{\text{مفقودة}}$
سيكون Forward. اجبارية

* $\underbrace{A}_{} + B \rightleftharpoons C + D$
اذا كانت مفقودة.
سيكون (backward).

example.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 - \quad K_c = 2 \text{ at } 375°C$$

$N_2 = 0.249$ mol
$H_2 = 3.2 \times 10^{-2}$
$NH_3 = 6.42 \times 10^{-4}$
$\Big]$ 3.5 L

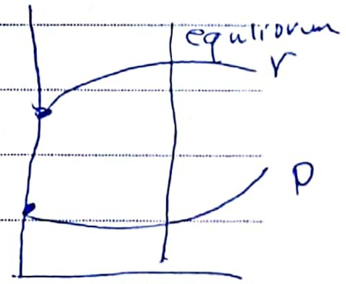
* معظم المسائل
بتركز
هون
بتوقعه بيروح
علاقة المولار

calculs

$$[H_2] = \frac{3.2 \times 10^{-2} \text{ mol}}{3.5 \text{ L}} = 9.17 \times 10^{-3} M$$

$$[N_2] = \frac{0.249}{3.5} = 0.0711 M$$

$$[NH_3] = \frac{6.42 \times 10^{-4}}{3.5} = 1.83 \times 10^{-4} M.$$

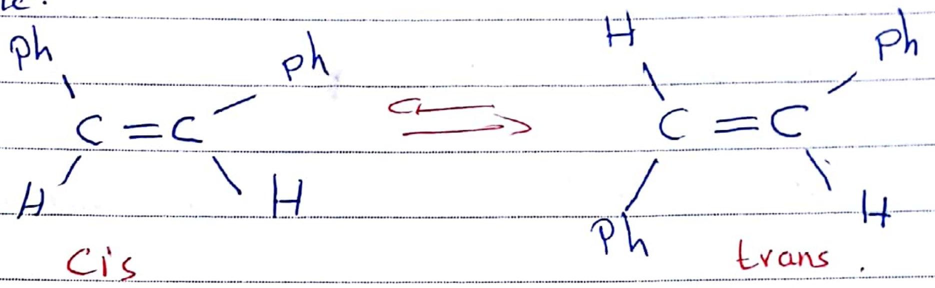


$$Q_c = \frac{[NH_3]_0^2}{[N_2]_0 [H_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.711) \times ((9.17) \times 10^{-3})^3} = 0.611$$

$Q_c < K_c$, so the rxn is procced: Forward.

③ Calc Conc. at equilibrum

example.



cis trans.

$K_c = 24.0$ at 200°C

$[cis]_0 = 0.850$ M

$[trans]_0 =$ Zero

	cis $\rightleftharpoons$	trans
initally	0.850	0
equilivrum	(0.850 − x)	x

$K_c = 24 = \frac{[trans]_e}{[cis]_e}$

$24 = \frac{x}{0.850 - x}$

$24(0.850 - x) = x$

$\boxed{x = 0.816 \text{ M}}$

$\rightarrow [cis]_e = 0.850 - 816 = 0.034$ M

$[trans]_e = 0.816$ M

* لايجوز أن يكون التركيز سالب

No.

example: $H_2(g) + I_2 \rightleftharpoons 2HI$ $K_c = 54.3$ at 470°C

If we started with 0.5 M of H_2 and I_2

$$H_2 + I_2 \rightleftharpoons 2HI$$

inially. 0.5M | 0.5 M | zero

$0.5 - X$ | $0.5 - X$ | $+2X$

لأنه من المعادلة أعدادها - نسبة استهلاك (H_2) و (I_2) متساوي //

$$K_c = 54.3 = \frac{(2x)^2}{(0.50 - x)^2}$$

$$\sqrt{54.3} = \frac{2x}{0.50 - x}$$

$X = 0.393$ M

$[I_2]_e = 0.5 - 0.393 =$

$[H_2]_e = 0.5 - 0.393$

$[HI]_e = 2.0393$ M

calculs

Example.

$$H_2 + I_2 \rightleftharpoons 2HI$$

i [0.00623 M] [0.00414 M] [0.0224 M]

$K_c = 54.3$, $T = 470^\circ C$

$$Q_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{(0.0224)^2}{(0.00414)(0.00623)} = 19.5$$

↓

The rxn proceed in the forward direction

* What is the conn. in the eqilibrum ?

[H_2] [I_2] [HI]

e (0.0623 - x) (0.06414 - x) 0.0224 + 2x

$$54.3 = \frac{(0.0224+2x)^2}{(0.00623-x)(0.00414-x)}$$

$$\overbrace{50.3x^2}^{a} - \overbrace{0.654}^{b}x + \underbrace{8.98\times10^{-4}}_{c} = \text{zero}$$

$\boxed{\text{Solution}}$

$$x = \frac{-b \mp \sqrt{b^2 - 4ac}}{2a}$$

لأن قيمة أكبر من التركيز الأصلي . a. Wrong

x = 0.0114 M ✗

$\boxed{x = 0.00158 \text{ M}}$ ✓

No.

* Factors effecting the equilibrium

Le Chateleirs Principle.

if an external stress is on a system that is at equilibrum, The System adjusts so that the stress is partially a fest and try to reach equilibrium again.

⇒ **stress** ⇒ change in concentration or in pressure or in temp.

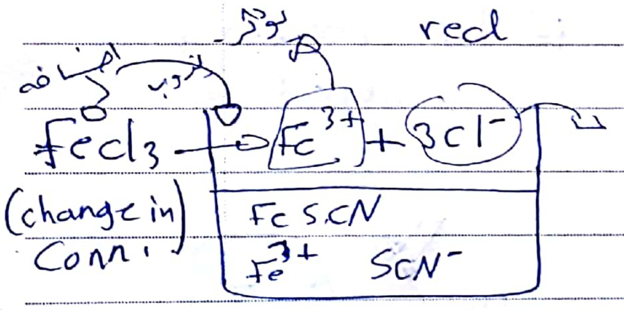
example ⇒

$FeSCN^{2+} \rightleftharpoons Fe^{3+} + SCN^-$

red yellow colorless

"Common ion" effect.

like Fe^{3+}, SCN^- تؤثر في الاتزان.



لا يؤثر على حالة الاتزان

زادت قيمتها.

$$Q_c = \frac{[Fe^{3+}][SCN^-]}{[FeSCN^{2+}]} > K_c$$

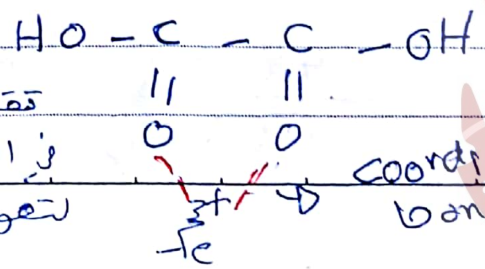
So, * rxn shifts in the backward direction

Conc

* of $FeSCN^{2+}$ increases

* concentration SCN^- decrease.

⇒ oxalic acid



$$HO-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH$$

عند اضافة

تقل نسبة (Fe^{3+}) الموجودة بشكل م

في الوعاء فالتفاعل يصبح اتجاه اماميا

لتعويض النقص في (Fe^{3+})

⇒ coordinate bond (تشاركية)

* Factors effecting the equilibrium

Le chateleirs Principle.

if an exteral stress is on a system that is at equilibrum, The System adjusts so that the stress is partally a fest and try to reach equlibrium again.

⇒ stress ⇒ change in concentration or in pressure or in temp.

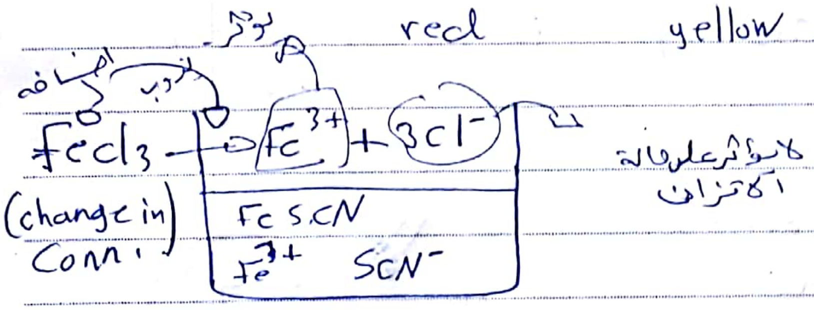
"common ion effect."

example ⇒

$$FeSCN^{2+} \rightleftharpoons Fe^{3+} + SCN^-$$

red yellow colorless

⇒ like Fe^{3+}, SCN^- تؤثر في الاتزان.



زادت قيمتها.

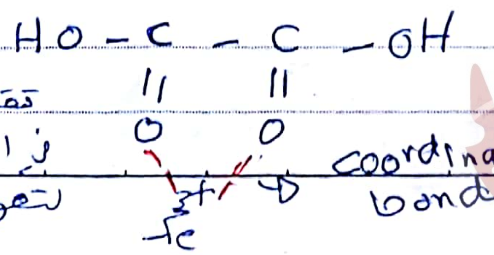
$$Q_c = \frac{[Fe^{3+}][SCN^-]}{[FeSCN^{2+}]} > K_c.$$ So, * rxn shifts in the backward direction

Conc

* of $FeSCN^{2+}$ increases

* concentration SCN^- decrease.

⇒ Oxalic acid



$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$

عند اضافة

تقل نسبة (Fe^{3+}) الموجودة بشكل م

في الوعاء فالتفاعل يصبح اتجاهه اماميا

لتعويض النقص في (Fe^{3+})

⇒ coordinate bond (تشاركية)

No.

* في المثال السابق لا يؤثر تغير الضغط لأن المواد ليست غازية فلا تتأثر بالضغط وتغيراته

factor affecting the equilibrium.

1- Change in conc.

2- Change in press : affects equlibrium if gases. exist.

$$PV = nRt$$

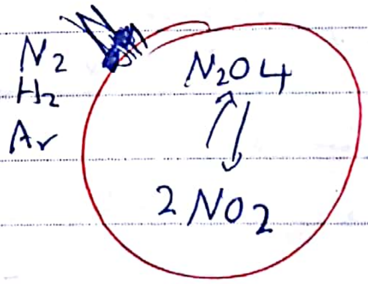
$$P = MRT$$

$$P \propto M$$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ if the pressure is doubled.

$\longleftarrow$

* how to increase the pressure.
  * decrease the volume
  * add another gas.



at equilibrium $[N_2O_4]_e$, $[NO_2]_e$

inc مضاعفة الضغط

$[N_2O_4]_0 = 2[N_2O_4]_e$ [illegible]

$[NO_2]_0 = 2[NO_2]_e$

$$Q_c = \frac{[NO_2]_0^2}{[N_2O_4]_0} = \frac{4[NO_2]_e^2}{2[N_2O_4]_e} = 2K_e$$

* $PCl_{5(g)} \rightleftharpoons Cl_{2(g)} + PCl_{3(g)}$

IF press is increased the rxn shifts in the backword direction.

* $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$

if pressure is increased → No effect because $\boxed{\Delta n = \text{zero}}$

* $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

if the pressure increases the rxn backwards

$\Delta H = (-)$

$A \rightleftharpoons B$

$A \rightleftharpoons B + \text{energy}\uparrow$

* Effect of temp

Effect of catalyst

* cat does not effect the equilibrum
* cat speed up the rxn to reach the equilibrum

$A \rightleftharpoons B$ K_{c1}

$B \rightleftharpoons C$ K_{c2}

$A \rightleftharpoons C$ $K = K_{c1} \times K_{c2}$

No. Chapter 16

Acids and bases

* Bronsted acids: substance donats Protons.

* " bases: " accepts a protons.

* $\underbrace{HCl}_{\cancel{\text{strong}}\ \text{acid.}} + H_2O \rightarrow Cl^- + H_3O^+$

* $\underbrace{CH_3COOH}_{\text{weak acid.}} \xrightleftharpoons{+H_2O} \underset{\text{con base}}{CH_3COO^-} + \underset{\text{con acid.}}{H_3O^+}$

* $\underset{\text{"base"}}{CH_3COO^-} + \underset{\text{"acid"}}{H_3O^+} \rightleftharpoons CH_3COOH + H_2O$

⇒ conjugate pairs :- CH_3COOH / CH_3COO^-

acid conj base.

⇒ H_2O / H_3O^+

base conj acid.

example.

$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{conacid}}{NH_4^+} + \underset{\text{coj base.}}{OH^-}$

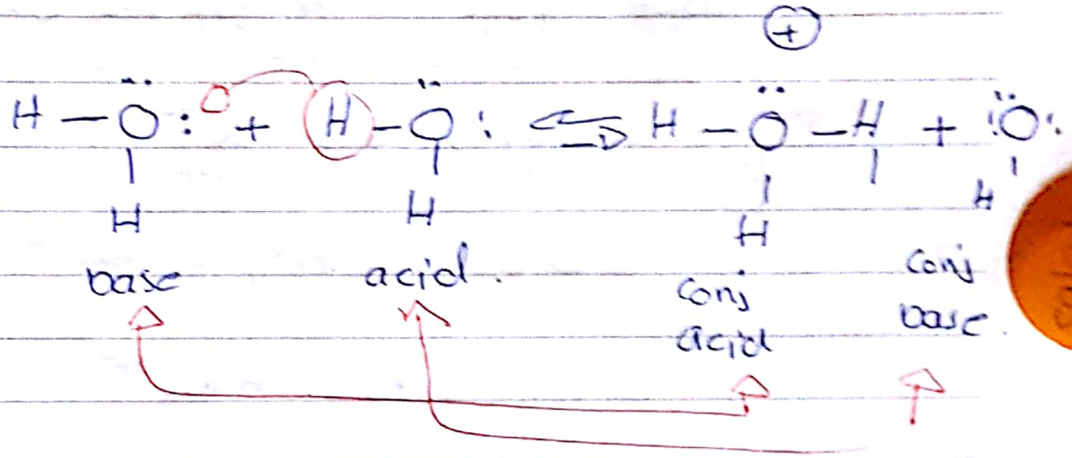
example

$\underset{\text{acid}}{HF} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{Conj base}}{F^-} + \underset{\text{Conj acid}}{H_3O^+}$

I acid-base properties of water

⇒ water act as a base and acid.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$



⇒ experimentally for pure water at 25 °C concentration of H_3O^+ is found $= 10^{-7}$ M

" " OH^- " " $= 10^{-7}$ M

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \Rightarrow K_W = [H^+][H_3O[OH^-]$$

$$K_W = (10^{-7})(10^{-7}) = 10^{-14}$$

⇒ $K_W = 10^{-14}$ at 25C°

↳ ion product constant.

when ever $[H^+] = [OH^-]$ ⇒ neutral Solution

$[H^+] < [OH^-]$ ⇒ basic

$[H^+] > [OH^-]$ ⇒ acidic

No.

example NaOH Solution with conc. = 0.0025 M
Calculte [H+] and [OH-]

Solution $NaOH \rightarrow Na^{+} + OH^{-}$

NaOH : Strange electrolyte ⟹ $[OH^{-}] = 0.0025 M$

acid

$$\boxed{K_W = [OH^{-}][H^{+}] = 10^{14-}}$$

$$= (0.0025)[H^{+}] = 10^{-14}$$

$$[H^{+}] = 4 \times 10^{12-}$$

pH ⟹ It is a measure of acidity.

-log ← p, H → [H+]

$$\underbrace{pH = -\log[H^{+}]}_{\text{علاقة عكسية}}$$

pH scale = (0 - 14) ⟹ $\underbrace{0 - 7}_{acid}$ - $\overset{netral}{7}$ - $\underbrace{-14}_{basic}$

what is the pH of HCl Solution (~~0.2~~ (0.10 M) ?

$HCl \rightarrow H^{+} + Cl^{-}$

$$pH = -\log(0.1)$$
$$= 1$$

② F [HCl] = 0.001 $pH = -\log(0.001) = 3$

⟹ what is the pH of pure water

$[OH^-] = [H^+] = 10^{-7}$

$pH = -\log(10^{-7}) = 7$

P OH ⟹ measure of basicity.

$POH = -\log[OH^-]$

example. what is the POH of Hcl solution (0.1 M)

Solution

$[H^+] = 0.1\ M$

$Kw = [H^+][OH^-] = 10^{14-}$

$[OH^-]\ 0.1 = 10^{-14}$

$\boxed{[OH^-] = 10^{-13}}$

$POH = -\log(10^{-13})$

$= 13$

$\boxed{PH + POH = 14}$; For the same Solution

$[OH^-][H^+] = 10^{-14}$

$-\log[OH^-] - \log[H^+] = -\log 10^{-14}$

$\boxed{POH + PH = 14}$

example

$[H^+] = 3.2 \times 10^{-4}$ M   pH ؟؟ pOH ؟؟

$pH = -\log(3.2 \times 10^{-4})$

$= 3.49$

$pOH + pH = 14$

$pOH = 10.51$

another example.

$[HCl] = 2.0$ M

$pH = -\log[H^+] = -\log(2.0) = (-0.30)$

$pH + pOH = 14$

$pOH = (\cancel{14}.3) \Rightarrow$ (14.تقريبا)

Strengh of acids and Basis.

⇒ most of the acids and basis are weak

Strong acid	Strong basis
HCl	MOH M: Alkali metal Li Na K ⋮
HBr, HI	$Ba(OH)_2$
$HClO_4$	$Sr(OH)_2$
HNO_3	
H_2SO_4	

weak acid	weak basis
CH_3COOH	NH_3
HF	$Ca(OH)_2$
H_2CO_3	$Al(OH)_3$
	$CaCO_3$

table 16.2 منقط

$$\underset{\text{acid}}{\overset{\text{strong}}{HCl}} + \underset{\text{bais}}{H_2O} \rightarrow \underset{\text{conject acid.}}{\overset{\text{we.}}{H_3O^+}} + \underset{\text{conject basi}}{\overset{\text{weak}}{Cl^-}}$$

very very weak.

$$\underset{\text{acid.}}{CH_3COOH} + \underset{\text{base.}}{H_2O} \rightleftharpoons \underset{\text{conj base}}{CH_3COO^-} + \underset{\text{conj acid}}{H_3O^+}$$

weak

weak

Conje pairs properties.

⇒ 1. If the acid is strong, then the conj base is very weak.

⇒ 2- The strongest acid in aqueous solution is H_3O^+

- The " bais in " " is OH^-

$$NaOH \rightarrow Na^+ + OH^-$$

يتفكك كامل لأن (OH^-) ~~[illegible]~~ لا يسمح أن يبقى قاعدة أقوى منه)
يسمح أن يبقى قاعدة أقل كلو لماهو أضعف منه.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

تبقى القاعدة في الوعاء لأنها أضعف من (OH^-)

No.

example what is the PH and POH of 1×10^{-3} M $Ba(OH)_2$

$Ba(OH)_2 \rightarrow Ba^{2+} + \underline{2}OH^-$

$[OH^-] = 2 \times 1 \times 10^{-3} = 2 \times 10^{-3} M$

$POH = -\log [2 \times 10^{-3}) = 2.7$

$POH + PH = 14$

$PH = 14 - 2.7 = 11.3$

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_a = \frac{[A^-][H^+]}{[HA]} \qquad \Rightarrow [H^+] = [H_3O^+]$$

→ acid (تفكك) dissociation constant

higher the "Ka value", the stronger the acid.

example- what is the $[H^+]$ of 0.5 M HF solution

$K_a = 7.1 \times 10^{-4} \Rightarrow$ 'weak acid'

No.

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

	HF	H_2O	F^-	H_3O^+
initally	0.5	constant.	0	0
equilib	$0.5-x$	〃	x	x

$$7.1\times10^{-4} = \frac{x^2}{(0.5-x)}$$

Solution

assume x is small with respect $0.5 \Rightarrow 0.5-x \simeq 0.5$

calcuis

$$7.1\times10^{-4} = \frac{x^2}{0.5} \Rightarrow x = 0.019\,M = [H^+] = [F^-]$$

test the result : $\frac{0.019}{0.5}\times 100\% = 3.8\%$ نسبة التفكك .

If the test $<5\% \Rightarrow$ test passed.

〃 〃 〃 $>5\% \Rightarrow$ test failed.

يمكن اعتماد هذا حل في حالة اذا كان test passed غير ذلك يجب حل المعادلة

كاملة دون إهمال قيمة X الي في المقام."

اذا كان $[HF] = [0.05]$

$$0.05 \quad Ka = \frac{x^2}{(0.05-x)} \quad x = 6.\times10^{-3}$$

احيانا

اذا عرفنا 5X

test $= \frac{6.10^{-3}}{0.05}\times 100\% = 12\%$ test faild.

$$7.1\times10^{-4} = \frac{x^2}{(0.05-x)} \Rightarrow x^2 = 3.5\times10^{-5} - 7.1\times10^{-4}\,x$$

$$\underset{a}{x^2} + \underbrace{7.1\times10^{-4}}_{b}\,x - \underbrace{3.5\times10^{-5}}_{c}$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$x = -6.2\times10^{-3}$

or $= 0.00557$

No.

How to determine the ka from the pH ?

example pH value of formic acid (0.10M) = 2.39
what is ka for the formic acid?

$$\begin{array}{lccc} & HA \rightleftharpoons & H^+ & + A^- \\ \text{inially} & 0.1 & \text{zero} & \text{zero} \\ \text{equilibrium} & 0.1 - x & x & x \end{array}$$

$$2.38 = -\log \overbrace{[H^+]}^{x}$$

$$x = 10^{-2.38}$$

$$[H^+] = x = 4.1 \times 10^{-3} M$$

$$ka = \frac{(4.1\times10^{-3})^2}{(0.1 - 4.1\times10^{-3})} = 1.8 \times 10^{-4}$$

التأين

Percentage of ionization (% ionization)

How much the acid will dissociate.

$$\% \text{ ionizition} = \frac{\text{ionized acid at equilibrium}}{\text{initial conc. of acid}} \times 100\%$$

$$\% \text{ ionization} = \frac{x}{\text{intial conc.}} \times 100\%$$

No.

calculs

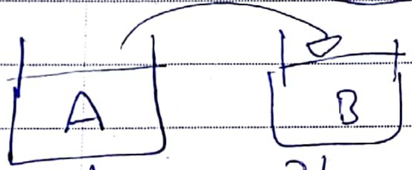
* di and Poly Protic acid.

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ $Ka_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

$H_2CO_3 \rightleftharpoons H_1^+ + HCO_3^-$ $Ka_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$

$Ka_1 \neq Ka_2$ $Ka_1 > Ka_2 > Ka_3 \dots$



2L 3L

3M 4M

after mixing

total volume = 2+3 = 5 L

ةتنقصه الذيب (الماد).

$\times$ $[A]_{new} = [A]_{old} \times \frac{2}{5}$

$\times$ $[B]_{new} = [B]_{old} \times \frac{3}{5}$

$\boxed{\text{ملاحظة}}$

$\Rightarrow$ عدد مولات قبل

=

بعد // //

example. $H_2C_2O_4$ (0.1 M), cla conc. of all ions at equilibrum?

$Ka_1 = 6.5 \times 10^{-2}$

$Ka_2 = 6.1 \times 10^{-5}$

$H_2C_2O_4 + H_2O \rightleftharpoons HC_2O_4^- + H_3O^+$

i	0.1	0	0
e	0.1 - X	X	X

No.

$6.5 \times 10^{-2} = \frac{x^2}{0.1 - x}$: assume 0.1 M = 0.10

6. $\Rightarrow x = 8.1 \times 10^{-2}$ M

$\boxed{\text{test}}$ = $\frac{8.1 \times 10^{-2}}{0.1} \times 100\%$ = 81 % fail

$6.5 \times 10^{-2} = \frac{x^2}{(0.1 - x)}$

$x^2 + 6.5 \times 10^{-2} x - 6.5 \times 10^{-3} = 0$

$x = 0.054$ M

الاتزان الثاني

e $\cancel{0.1}X < \cancel{0}.054$

$H_2C_2O_4^- + H_2O \rightleftharpoons C_2O_4^{-2} + H_3O^+$

i 0.054 0 0.054

e 0.54 - y y 0.054 + y.

~~0.054 + y~~

$6.1 \times 10^{-5} = \frac{(y)(0.054 + y)}{(0.054 + y)}$

assume $0.054 - y \approx 0.054$

$0.054 + y \approx 0.054$

$6.1 \times 10^{-5} = \frac{\cancel{0.054}(y)}{(\cancel{0.054})}$

test : $\frac{y}{0.054}$ = 0.11% passed.

No.

$$\boxed{y = 6.1 \times 10^{-5}\ M}$$

Weak basis

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$\underbrace{K_b}_{} = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

→ base ionization constant.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \boxed{\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}}$$

x

* $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$$K_b = \boxed{\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}}$$

$$K_a \times K_b = [OH^-][H^+] = K_w$$

calculs

Factors affecting the acidity :-

1- Conncentration
2- Type of the acid //
3- temp
4- Solvent .

two type of acid : ① Hydrohalic acid

$$\underbrace{Hcl, HBr, HI, HF}_{X-H}$$

polarity

$HF > Hcl > HBr > HI$

strong — weak

Bond Strength

$HF > Hcl > HBr > HI$

weak — strong

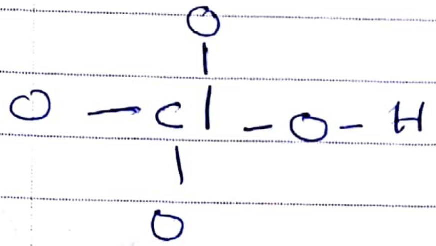
primarly : hydrohalic acid follow the strengh of the bond to determine the strengh of the acid .

two factor => ① polarity ② Bond strengh
تأثيرها بيطغى على تأثير ال Polarity .

② Oxacids .

الأقوى $Hclo_4 > Hclo_3 > Hclo_2 > Hclo$ الأضعف

No.



$O-Cl(O)(O)-O-H$

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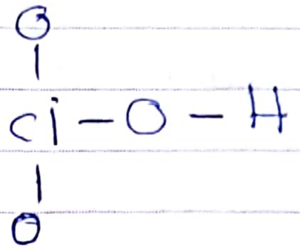


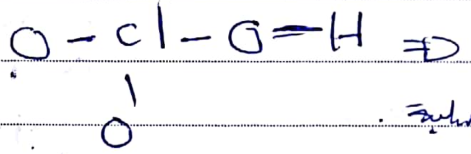
$Cl(O)(O)-O-H$

$O-Cl-O-H$ ، $Cl-O-H$

⇒ by increasing number of surrounddng oxygens the O–H bond become weaker and so the acid is stronger (assuming the same central atom)

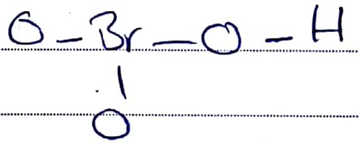
calculus

$HClO_3$,
$HBrO_3$
HIO_3 .

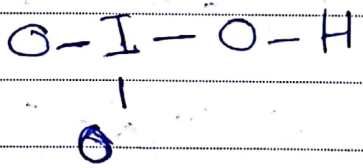


$O-Cl(O)-O-H$ ⇒

الأقوى لأن
الإجابة Cl ـ O
أقوى لأن أعلى كهروسلبية .



$O-Br(O)-O-H$



$O-I(O)-O-H$

$HNO_3 > HNO_2$ ، $HClO$ ، $HBrO$ ، HIO

أقوى لأن عدد ذرات ال O أكبر .

الأقوى لأن Cl أعلى كهروسلبية .

No.

$Nacl \rightarrow No^{+} + cl^{-}$

محايد

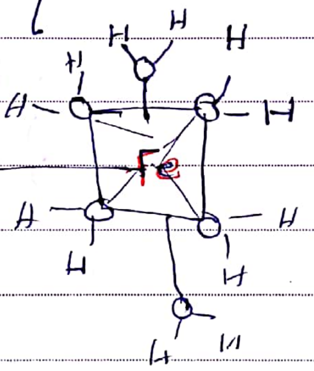
Metal ions hydrolysis

metal ions with large positive charge (> 3) reacts with water to make an acid.

$fecl_3 + H_2o \rightarrow Fe^{3+} + 3Cl^{-}$

$AlCl_3 \rightarrow Al^{3+} + 3Cl^{-}$

$Fe^{3+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+}$



روابط تناسقية.

يتصرف كحمض

$[Fe(H_2O)_5OH]^{+2} + H^{+} \rightarrow [Fe(H_2O)_4(OH)_2]^{+} + H^{+}$

$[Fe(H_2O)_3(OH)_3] + H^{+}$

* $CH_3COONa \rightarrow \underset{\text{very very weak.}}{Na^+} + \underbrace{CH_3COO^-}_{\text{weak acid.}}$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underbrace{OH^-}$

basic solution.

* $NH_4Cl \xrightarrow{H_2O} NH_4^+ + Cl^-$

$\rightarrow NH_4^+ + H_2O \rightleftharpoons NH_3 + \underbrace{H_3O^+}$

acidic solution.

calculs

* $CH_3COONH_4 \xrightarrow{H_2O} CH_3COO^- + NH_4^+$

$CH_3COO^- + H_2O \rightarrow CH_3COH + OH^-$ Kb

$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ Ka

if Kb > Ka = the solution is basic

Ka > Kb " " " acidic.

Ka = Kb " " " neutral.

Amphotiric oxides

oxides that react as an acid or a base. in water

$Na_2O + H_2O \rightarrow 2NaOH$ it is not amphotiric

قاعدة $\underbrace{Al_2O_3} + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$\underbrace{Al_2O_3}_{\text{حمض}} + H_2O + 2NaOH \rightarrow 2NaAl(OH)_4$

لذا يسمى amphotiric

$\boxed{H_2PO_4^-} \Rightarrow$ لا يعتبر (amp.) لأنه ليس "oxides"

$NaNO_3$ —	neutral
K_2O	basic
$CrCl_3$	acidic

$NH_4F \rightarrow NH_4^+ + F^-$ iF has Kb so acidic.

Lewis acids and basis

Lewis acid: accept e^-

" bais donate. e^-

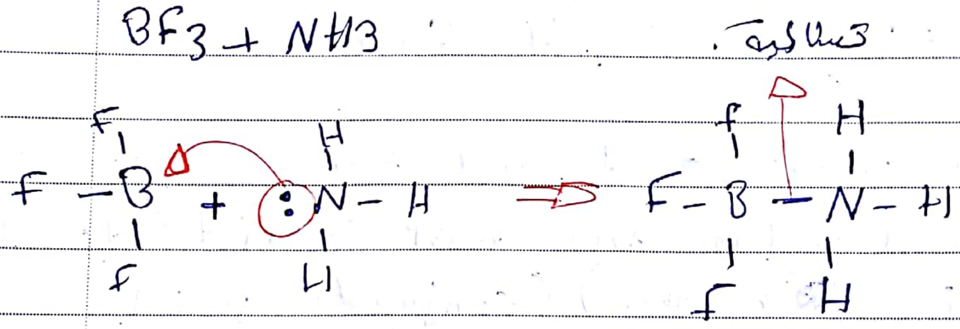
* $NaOH + HCl \rightarrow NaCl + H_2O$

$\cancel{Na^+} + OH^- + H^+ + \cancel{Cl^-} \rightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O$

$\underset{\text{Lewis base}}{OH^-} + \underset{\text{Lewis acid.}}{H^+} \rightarrow H_2O$

$H-\ddot{\underset{..}{O}}: + H \rightarrow H-O-H$

$BF_3 + NH_3$

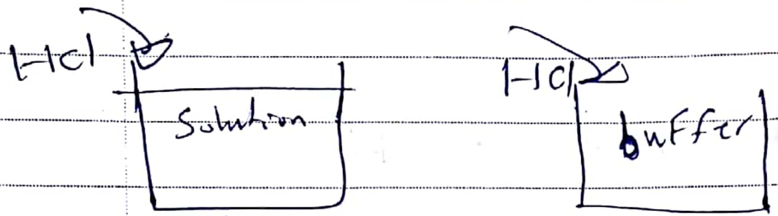


calculs

chapter 17

buffer solution:

solution that resist changes in pH



pH=7 | pH=7

بعدالإضافة pH=2 | pH=6.9

* must contain acid and bais.

* The acid and the bais must coexist (donot neutralize each other) (conjugate pair).

*To make a buffer Solution mix CH_3COOH with CH_3COONa.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

i	$[AH]_0$	$[A^-]_0$	0
e	$[HA]_0$	$[A^-]_0$	

No.

Buffer capacity :

CH_3COOH +	CH_3COONa	
1M	0.1M	تقاوم القاعدة أكثر
0.1 M	1M	〃 الحمض 〃
1 M	1M	تقاوم الحمض مثل القاعدة
0.1M	0.1 M	〃 〃 〃 〃

كفاءة أعلى لأن تراكيز أعلى

calculs

The effectivness of the buffer Solution
- prepared with high Conc.
- 〃 with equal amounts of acid / conj base.

example.

KH_2PO_4	H_3PO_4	✓	
K_2HPO_4	H_3PO_4	✗	
$HClO_4$	$NaClO_4$	✗	حمض قوي
$C_5H_5NH_2$	C_5H_5NHCl	✓	

what is the pH a Solution made from 1M of CH_3COOH and CH_3COONa ($Ka = 1.8 \times 10^{-5}$)

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
i	1M	1M	0
c	1 - x	1 + x	x

$$1.8\times10^{-5} = \frac{x(1+x)}{1-x}$$

$$1.8\times10^{-5} \cong x$$

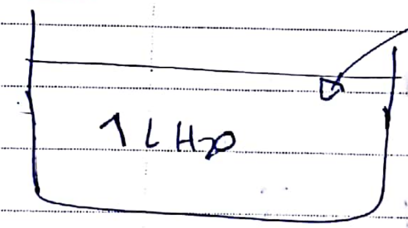
$x = 1.8\times10^{-5}\,M$ $\quad$ $pH = -\log(1.8\times10^{-5})$

$= 4.74$

* عند تحضير محلول منظم بنفس تركيز الحمض والقاعدة لا تتغير pH لأنها نسبة ثابتة

فقط الذي يتغير (buffer capacity)

$$\frac{x\boxed{(1+x)}}{\boxed{1-x}}$$



0.1 mole HCl

pH (water) = 7.0

after addition.

$HCl \rightarrow H^+ + Cl^-$

$[H^+] = 0.1\,M$

$pH = -\log 0.1 = 1$

$\boxed{\Delta pH = 6 \text{ unit}}$

without buffer solution.

if the 0.1 Mole of HCl is added to the previous buffer Solution, calc the ΔPH :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
i	1	1	0
[after added HCl]	1.1	0.9	0 →
e	1.1 − X	0.9 + X	X

تقل بنفس [0.1] وهو [HCl]

يتفاعل

$HCl + CH_3COO^- \rightarrow CH_3COOH + Cl^-$

تزيد

No.

$$1.8\times10^{-5} = \frac{x(0.9-x)}{(1.1+x)}$$

$$1.8\times10^{-5} \approx \frac{x(0.9)}{1.1}$$

$x = 2.2\times10^{-5}$ M = [H+)

pH = $-\log 2.2\times10^{-5} = 4.66$, ΔHp
= 4.74 - 4.66
= 0.08 unit

calculs

Preparing buffer solution with different pH values

$$HA \rightleftharpoons A^- + H^+$$

$$Ka = \frac{[H^+][A^-]}{[AH]}$$

$$pka = pH - \log\frac{[A^-]}{[HA]}$$

$$\boxed{pH = pka + \log\frac{[A^-]}{[AH]}}$$ Henderson's equation.

example : prepear buffer solution with pH = 7.4 from aceticaacid / acetate.

NaoL

$$7.4 = \underbrace{4.74}_{-\log 1.8\times10^{-5}} + \log\frac{[A^-]}{[HA]}$$

No.

$\frac{[A^-]}{[AH]} = 2.18 \times 10^{-3}$ Pour buffer capacity.

For a buffer Solution with high capacity.
choose acid / conj base where pka almost
equal the target pH

NaH_2PO_4 pka = 7.21

$H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+$

$NaH_2PO_4 + Na_2HPO_4$

$7.4 = 7.21 + \log \frac{[A^-]}{[AH]}$

$\frac{[A^-]}{[AH]} = 1.5$

Solubility equilibrim

NaCl AgCl

$NaCl \rightarrow Na^+ + Cl^-$

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$ → تركيز ثابت
لانها صلبة

No.

$[AgCl]_{(s)}$ $K_c = [Ag^+][Cl^-]$

$K_{sp} = [Ag^+][Cl^-]$

solubility.
product
constant.

$K_{sp}(NaCl) > K_{sp}(AgCl)$

⇒ as Ksp value increases, the solubily increase.

	(Ksp)
CdS	$8.\ 10^{-28}$
FeS	6.0×10^{-19}
PbS	3.4×10^{-28}

solubility: FeS >> CdS > PbS.

* $MgF_2 \rightleftharpoons Mg^{2+} + 2F^-$

$K_{sp} = [Mg^{2+}]_c [F^-]^2_c$

* $Ca_3(PO_4)_2 \Rightarrow K_{sp} = [Ca^{2+}]^3_e [PO_4^{3-}]^2_e$

$Q = [Ca^{2+}]^3 [PO_4]^2$ at non-Sat equilibrium conc.

*

calculus

$Q > K_{sp}$ super saturated.

$Q < K_{sp}$ unsaturated.

$Q = K_{sp}$ saturated.

*تكون (Ksp) مناسبة للمقارنة بين قوة اذابة المركبات عندما
تكون المركبات جميعا تعطي نفس عدد الايونات مثل pbs
fes.

Molar Solubility.

number of moles dissolved to make saturate. solution in unit volum 1L ; 100 mL.

$$ZnS \rightleftharpoons Zn^{2+} + S^{2-}$$

Solubility:

number of grams of solute dissolved to have a saturte Solution Per unit volum (1L or 100 mL)

molar Solubility x molar mass = Solubility.

No.

Example Solubility of $CaSO_4$ = 0.67 g/L
Find Ksp ?

$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{-2}$

moles of $CaSO_4$ dissolved . $\frac{0.67\ g}{136.2\ L}$. 4.9×10^{-3} mol/L
molar solubility

$K_{sp} = (4.9 \times 10^{-3})^2$ unitless

Example: K_{sp} for AgCl = 1.6×10^{-10}, Find its molar solubility.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10} = [X][X] =$

i 11/Tg 0 0

e X X

$x^2 = 1.6 \times 10^{-10} \Rightarrow x = \sqrt{1.6 \times 10^{-10}} = 1.3 \times 10^{-5}$ M

amount of AgCl dissolved to make 1L saturated solution
$= 1.3 \times 10^{-5}$ mole
Molar Solubility $= 1.3 \times 10^{-5}$ mol /L

calculs

example. ksp of $Cu(OH)_2 = 2.2\times10^{-20}$
calc molar soluibity.

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2\,OH^-$$

e $\quad X \quad 2X$

$$K_{sp} = [Cu^{2+}][OH^-]^2$$

$$2.2\times10^{-20} = X\,(2x)^2$$

$$2.2\times10^{-20} = 4x^3$$

$$\boxed{x = 1.8\times10^{-7}}$$

molar Solubility $= 1.8\times10^{-7}\ \frac{mole}{L}$

---

* example if 200. mL $BaCl_2$ (4.0×10^{-3} M) is mixed with 600.0 mL of K_2SO_4 (8.0×10^{-3})

ممكن يجي غير [illegible]

Solution:

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 + 2KCl.$$

$$Ba^{2+} + 2Cl^- + 2K^+ + SO_4^{-2} \rightarrow BaSO_{4(s)} + 2K^+ + 2Cl^-$$

$$Ba^{2+} + SO_4^{-2} \rightleftharpoons BaSO_{4(s)}$$

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+} + SO_4^{-2}$$

$$K_{sp} = [Ba^{2+}][SO_4^{-2}]$$

new conc. of $Ba^{2+} = 4.0\times10^{-3} \times \frac{200}{800} = 1\times10^{-3}$ M

// " " $SO_4^{-2} = 8.0\times10^{-3} \times \frac{600}{800} = 6\times10^{-3}$ M

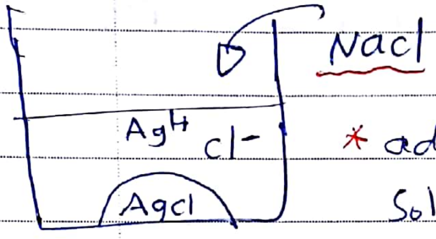
No.

$Q = 1.0 \times 10^{-3} \times 6 \times 10^{-3} = 6 \times 10^{-6}$

$Q > K_{sp}$ ppt will form

Common ion effect.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$



* adding Cl^- will decreasing the Solubility of AgCl

* Adding Ag^+ will decreasing the Solubility of AgCl.

in this case common ion Ag^+ and Cl^-

Example. calculate the Solubility of AgCl in 6.5×10^{-3} M $AgNO_3$ ($K_{sp}(AgCl) = 1.6 \times 10^{-10}$)

$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

i مادة صلبة لا يهم التركيز 6.5×10^{-3} 0

e — — // $6.5 \times 10^{-3} + X$ X

$K_{sp} = [Ag^+][Cl^-]$

$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + X)(X)$ ممكن اهمالها

لأن التركيز القادم من AgCl قليل جداً %

No.

$1.6\times10^{-10} = (6.5\times10^{-3})\ X$

$X = 2.5\times10^{-8}$ M ⇒ molar Solubility

Solubility $= 2.5\times10^{-8}\times 143.4 = 3.6\times10^{-6}$ g/L

Molar Soluibity without $AgNO_3$ $= \sqrt{KSP}$

$= 1.3\times10^{-5}$

Solubility $= 1.3\times10^{-5}\times 143.4 = 1.8\times10^{-3}$ g/L

Chapter 18 Thermolynamics II

Spontaneous process ⇒ ① evaportion of water عمليات تحدث تلقائية (endo)
nonspontaneous process ② Rust صدأ (endo)
③ salt in water (exo)
④ waterfalls. (exo)
⑤ Ice melting (endo)
if $T>0$

⇒ there is no relation between enthalpy change (ΔH) with Spontaneouity.

Entropy : * is a measured of disorderd.
* is a mesured of how energy is dispersed in different ways/state/

* طرق توزيع الطاقة كلما زادت تزيد entropy

higher dispersion → higher entropy.

Chapter 18 Thermolynamics II

Spontaneous process ⇒ ① evaportion of water (endo) عمليات تحدث تلقائياً
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higher dispersion → higher entropy.

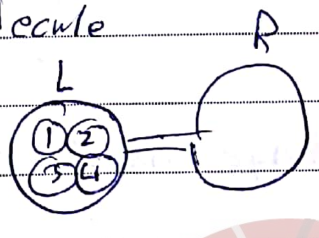
of states for transering One molecule

L	R
234	1
134	2
124	3
1234	4

4 ~~molea~~ micro states

L	R
1	234
2	134
3	124
4	123

4 microstates.



$$\underbrace{S}_{\text{entropy}} = K \ \text{lin}\ W$$

↳ number of microstates.

K ↓ Boltzman Constant.

$(1.38 \times 10^{-23}$

⟹ what is important is change in entropy (ΔS)

$$\Delta S = S_f - S_i$$

$$= K \text{lin} W_f - K \ \text{lin} W_i$$

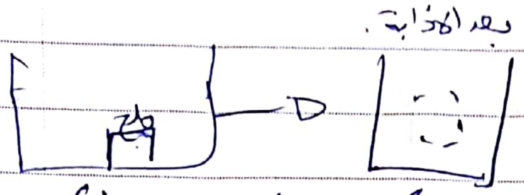
$$\boxed{\Delta S = K \ \text{lin} \frac{W_f}{W_i}}$$

not: ΔS can not be deterimned using W_f, W_i (لأنه صعب تحديد العدد.)
experiment (thermodymix) enable us to determine ΔS

$$S = K \ \underbrace{\text{lin} W}$$

entropy (S) can take the values
$(0 \rightarrow \infty)$ (Positive value)

Change inentropy (ΔS) can take negative and positive value.



$S_i < S_f$

$\Delta S = $ positive.

عمليات الإذابة دائمة تعطي فوضى أكثر.

* ice $\rightarrow$ liquid water

$S_i < S_f$ ΔS موجبة

* liquid $\rightarrow$ vapor

$S_i < S_f$ ΔS موجبة. * فوضى الأمن الحالة السابقة

calculs

entropy $\Rightarrow$ Solid $<$ liquid $\ll$ vapor.

$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$ $\Delta S_{(NaCl)} =$ موجبة

$\Delta H(H_2O) = (-)$ due to hydration shells.

~~Cl~~ محصلة الفوضى الناتجة عن NaCl أكبر من الترتيب الذي حدث في (H_2O) لذلك $\boxed{\Delta S = \text{موجبة}}$ لكل التفاعل.

standard entropy ($\Delta S°$)

entropy (changes) at standard conditions.

1 atm, 25°C, 1 mole, 1 molarity.

example: which of the Fellowing has greater ($S°$) value.

graphite $>$ dimonds.

He $<$ Ne عدد $\boxed{e}$ أكثر

* $Br_{(l)} < Br_{(g)}$

* $CH_4 < C_2H_6$

* $Suger_{(s)}$ ~~SD~~ $\rightarrow$ $suger_{(aq)}$ ΔS (+)

2nd ~~da~~ law of Thermo

* the entropy of univese increase in
* spontaneous changes
* $\Delta S_{univ} = zero$ in eqilibrum change.

universe = System + Surrounding

$$\Delta S_{univ} = \underbrace{\Delta S_{sys}}_{1st\ case} + \underbrace{\Delta S_{surr}}_{2nd\ case}$$

$$\Delta S_{system} = \Sigma n S_{prod} - \Sigma m S_{reactant}$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta S_{system} = (c.S_C + d.S_D) - (a.S_A + b.S_B)$$

example

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

S° 92.9 39.8 213.6 $\frac{J}{K.mol}$

No.

$$\Delta S^\circ_{rxn} = 1\times 39.8 + 1\times 213.6) - (1\times 92.9)$$
$$= \boxed{160.5\ \frac{J}{mol.K}}$$

example.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

S° 192 131 193 $\frac{J}{mol.K}$

$$\Delta S^\circ_{System} = (2.193) - (1\times 192 + 131\times 3) = \boxed{-199\ \frac{J}{mol\ K}}$$

example.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl(g)$$

$S^\circ =$ 131 223 187 $\frac{J}{K.mol}$

$$\Delta S^\circ_{system} = (2\times 187) - (223.131) = \boxed{+20\ \frac{J}{mol.K}}$$

If a rxn produces gases the ΔS° will be large and positive

If a change consumes gases then ΔS° will be large and negative

If a change keeps the number of moles of gases, then ΔS° will be small and $\boxed{+ \text{ or } -}$

No.

The main reasons for any high S

* $2H_2(g) + O_2(g) \rightarrow H_2O(l)$ (−) and large.

* $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ ± small

* $I_2(g) \rightarrow 2I(g)$ + and large.

entropy change for the surrounding

If we have an exothermic rxn / change.

لأن التفاعل طارد للحرارة. $-\Delta H_{sys} \propto \Delta S$ surr لأن زيادة درجة الحرارة تزداد الفوضى.

assume thermal equilibrum between sys and surr

$\Delta S_{surr} \propto \frac{1}{T_{surr}} \rightarrow T_{sys}$ نعوض

$\Delta S_{surr} \propto \frac{-\Delta H_{sys}}{T_{sys}}$

$\Delta S^\circ_{univ} = \left(\Sigma n S_{prod} - \Sigma m S_{react}\right) - \frac{-\Delta H_{system}}{T_{sys}}$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3$

$\Delta H^\circ_{rxn} = -96.6 \text{ kJ/mol}$ مهما أخذ رxn الحرارة.

$\Delta S^\circ = -199 \text{ J/mol.K}$

$\Delta S^\circ_{surr} = \frac{-\Delta H}{T} = \frac{96.6 \times 10^3}{298} = 311 \frac{J}{mol.K}$.

$\Delta S^\circ_{univ} = \Delta S_{sys} + \Delta S_{sur}$.

$= -199 + 311 = 112$

$$\Delta S^\circ_{univ} = \left(\sum n S_{Prod} - \sum m S_{react}\right) - \frac{\Delta H_{sys}}{T_{sys}}.$$

3ed law of thermo.

- $S \propto$ number of microstates $\boxed{S = k \ln W}$
- for a perfict crystal at 0K Then S= zero
  as temp increase, S increases

For important crystal (contain impurities) S will be greater then Zero

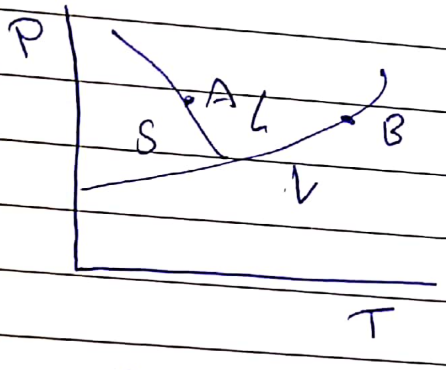
عند الوصول لحالة الاتزان تكون ΔG°_{rxn} تساوي صفر.

$$0 = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$0 = 177.8 \times 10^{+3} - T(160.5)$$

$$T = 1108K \Rightarrow 835^\circ C$$

phase transitions :



A: Solid-liqu equ

B: liq-vapor equ.

$\Delta G = \Delta H - T\Delta S \Rightarrow$ عند الاتزان تساوي صفر.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ مو شرط تكون صفر. '' ''

at $S \rightleftharpoons L$ equ

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\Delta S_{fuss} = \frac{\Delta H_{fuss}}{T_{fuss}} , \quad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$$

For point A   For point B

Calkulte ① ΔS_{fuss} ~~=~~ if $\Delta H_{fuss}(H_2O) = 6.0 \times 10^3$ J/mol

$$\Delta S_{fuss} = \frac{6.0 \times 10^3}{273} = 22.0 \ J/mol$$

② $\Delta H_v = \cancel{4}40.7 \times 10^3 \, J/mol$

$$\Delta S_{vap} = \frac{40.7 \times 10^3}{373} = 109.1 \, J/mol.K$$

~~ΔG~~ Free energy and equilibrium.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

AT equilibrum ⇒

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

example. clac K for the rxn

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

$\Delta G^\circ_f \quad -237.2 \quad 0 \quad 0$

$$\Delta G^\circ_{rxn} = -2 \times (-237.2) = 474.7 \, KJ/mol$$

$$\Delta G^\circ = -RT \ln K$$

$$474.7 \times 10^3 = -(8.314)(298)(\ln K)$$

$\ln K = -191.5$

$K = e^{-191.5} = 7 \times 10^{-84}$

example

K_{sp} (AgCl) = 1.6×10^{-16} clac. ΔG°

for AgCl $\rightleftharpoons$ $Ag^+ + Cl^-$

$\Delta G^\circ = -RT \ln K_{sp}$

$= -8.314 \times 298 \times \ln(1.6 \times 10^{-10})$

$= 56.$ KJ/mol

example.

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta G^\circ = 5.4 \times 10^3$ J/mol

$K_p = 0.113$ at 25 °C

if a mix of N_2O_4 and NO_2

$P = 0.122$ $P = 0.453$ atm

Calc ΔG . [illegible]

$\Delta G = \Delta G^\circ + RT \ln \underline{Q}$ J

$\Delta G = 5.4 \times 10^3 + 8.314 . 298 . \ln \left(\frac{(0.453)^2}{0.122} \right)$

$= (-) 3.06 \times 10^3$ J/mol

Five Apple

Chapter 19

19.2 electrochemical rxns.

Galvanic cell ⇒ electro chemical cell that produces electrisity spontaneously $\boxed{\Delta G = -}$

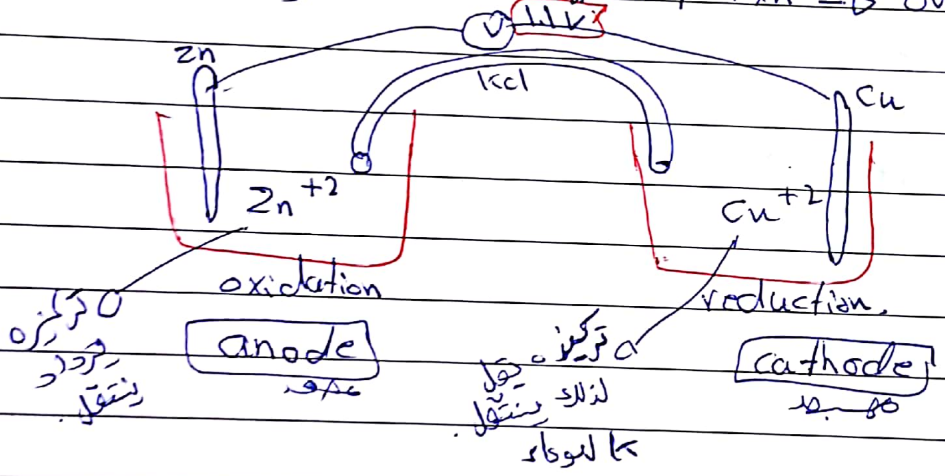
$$Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

* $Zn \rightarrow Zn^{+2} + 2e^-$ lost e^- (oxidation rxns.

$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ e^- gained. (reduction rxn)

each reaction is called half cell rxn.

Combining the two half cell rxn → over all rxn (Redox)



Danial cell

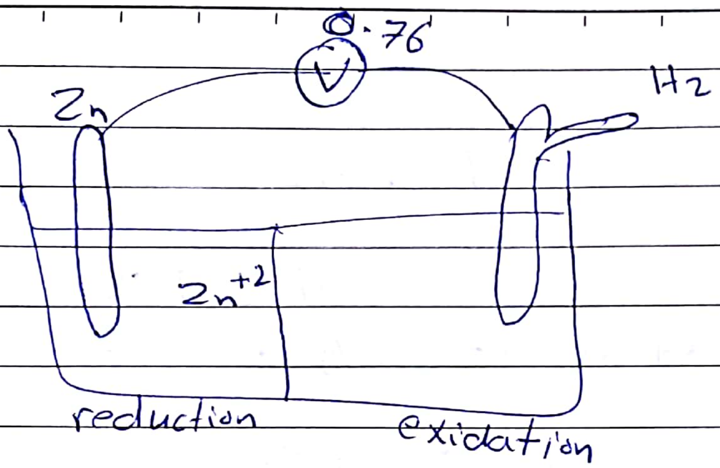
تتكون من Zn, Cu

هذا الفرق بينها وبين ال Galvanic.

measured voltage. (std) cell potential.

(std) electro motive force emf

$$E^0_{cell} = \underset{\text{1st half}}{E^0} + \underset{\text{2nd half}}{E^0}$$



E° anode = zero
cathode

$E_{cell} = E_{cath} - E_{anode}$

$0.76 = E_{Zn} - 0$

$E_{cath} = 0.76\ V$

$H_2 \rightarrow 2H^+ + 2e^-$

$Zn^{+2} + 2e \rightarrow Zn$

$H_2 + Zn^{+2} \rightarrow 2H^+ + Zn$

$E^{\circ} = E^{\circ}_{anode} + E^{\circ}_{cathod}$.

$Zn \rightarrow Zn^{+2} + 2e^{-}$ E_o = anode = ??

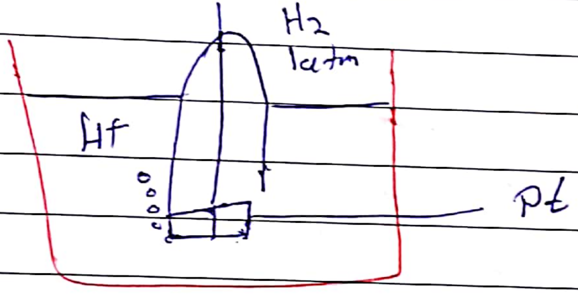
$Cu^{+2} + 2e^{-} \rightarrow Cu$ E° = cathode = ??

$Zn + 2e^{-} \rightarrow Zn$ E_o anode = -??

$Cu + 2e^{-} \rightarrow Cu$ E_o cathode = ??

$$\boxed{E^{\circ}_{cell} = E^{\circ}_{cathod} - E^{\circ}_{anode}}$$

SHE



* $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$.

⇒ all half cell rxns are written as a reduction rxns table (19.1)

اختزال .

example.

reduced form .

oxidized form ← $\boxed{F_2} + 2e^- \rightarrow \boxed{2F^-}$ $E^\circ = +2.87$

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ = zero$.

$\boxed{Li^+} + e^- \rightarrow \boxed{Li_{(s)}}$ $E^\circ = -3.05$

بتصير تاكسد .

$\boxed{E^\circ, \Delta G \quad \text{عكس الاشارة}}$

⇒ reduced form

⇒ oxidized form

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}.$$

cathode / $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ اختزال . $E^\circ = ~~-0.76~~ 0.34$

anode. بنعكس $Zn + 2e^- \rightarrow Zn_{(s)}$. $E^\circ = ~~+0.34~~ 0.76$

so ⇒ * half cell with the most positive. E° will keep its reduction rxn, and the other will get oxidized. (oxidatio)

$E^\circ_{cell} = 0.34 - (-0.76) = 1.1V$

* $Ag^+ + e \rightarrow Ag_{(s)}$ $E^o = 0.80$ V فولت cath
$Mg^{2+} + 2e^- \rightarrow Mg_{(s)}$ $E^o = -2,37$ V anode

for this Galvaniccell, Calc. $E^o_{cell} = ?$

$E^o_{cell} = E^o_{cath} - E^o_{anode}$.

$= 0.8 - (-2.37) = 3.17$ V

* over all rxns

$$Mg \cancel{+2e^-} \rightarrow Mg^{2+}_{(aq)} + \cancel{2e^-}$$
$$2Ag^+ + \cancel{2e^-} \rightarrow 2Ag_{(s)} \quad +$$

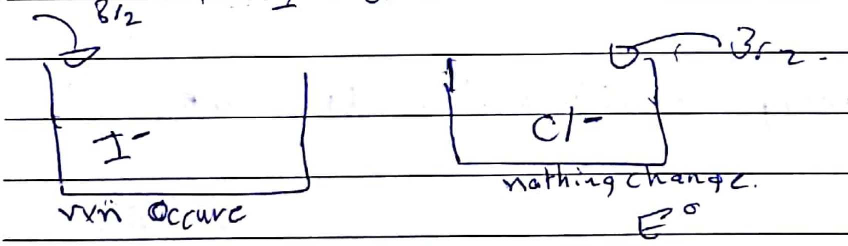
$$2Ag^+_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)}.$$

E^o is intensive property.

$Ag \rightarrow Ag^+ + e^- \Rightarrow E^o = -0.80$ V
$2Ag^+ + 2e^- \rightarrow 2Ag_{(s)} \Rightarrow E^o = 0.8$ V
نفس القيمة لل E^o

---

what will happen if Br_2 is added to NaI and NaCl Solution.



	E^o	
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36 V	⇒ most positive s. keep
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07 V	
$I_2 + 2e^- \rightarrow 2I^-$	0.53 V	

* How E° is releated to $\underbrace{\Delta G \text{ and } K}_{\text{thermodynamic}}$.

For a Galvanic cell

total charge passed = number of e^- × charge of one e^-

= moles of e^- × charge of one mole of e^-

Charge of mole of e^- = $\underset{\text{عدد افوغادرو .}}{6.022^{23}} \times \underset{\text{شحنة الالكترون الواحد.}}{1.6 \times 10^{-19}}$ C = كولوم .

$$= \underbrace{96485}_{\text{Faraday constant (F)}} \frac{C}{mol}$$

(total charge passed = $\underset{\text{عدد المولات -}}{\underline{\underline{n}}}F$)

* E°_{cell} : max Votage measured of a Galvanic cell, which is the work done by charged passed.

* $E^\circ_{cell} = \frac{\textcircled{-} W_{ele}}{nF}$ because done by charged

$$W_{ele} = -(nF)(E^\circ_{cell})$$

⇒ Gibbs energy : energy available to do work.

$$\boxed{\Delta G^\circ = W_{ele}}$$

$$\Delta G = -nF(E^\circ_{cell})$$

From Chapter 18 $\Delta G^\circ = -Rt \ln K$

$Rt \ln K = nFE^\circ$

$$\boxed{E^\circ = \frac{Rt}{nF} \ln K}$$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$\Delta G^\circ = -nFE^\circ$

$\Delta G = -nFE$

$E^\circ = \frac{Rt}{nF} \ln K$

* $2Au_{(s)} + 3Ca^{+2} \rightarrow 2Au^{+3} + 3Ca(s)$

Calc ΔG° and K

anode (oxidation) $Au^{+3} + 3e^- \rightarrow Au(s)$ $E^\circ = 1.50\ V$

cathode (reduction) $Ca^{+2} + 2e \rightarrow Ca(s)$ $E^\circ = -2.87\ V$

$E^\circ_{cell} = -2.87 - 1.5 = \underline{\underline{-4.37\ V}}$

غير تلقائي

n= (عدد الإلكترونات)

$\Delta G^\circ = -nFE^\circ$

$= -6 \times 96485 \times -4.37 = \underline{253\ kJ/mol}$

ΔG° [illegible]

63,64,77,81,82

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q \rightarrow$$ بالقسمة على $-nF$

$$\boxed{E = E^\circ - \frac{RT}{nF} \ln Q}$$ قانون عام.

example.

$$Co + Fe^{+2} \longrightarrow Co^{+2} + Fe$$

anode. $Co^{+2} + 2e^- \rightarrow Co \qquad E^\circ = -0.28\ V$

$\underbrace{\text{Cathode}}_{\text{حسب المعادلة}}$ $Fe^{2+} + 2e \rightarrow Fe \qquad E^\circ = -0.44\ V$

$$E^\circ_{cell} = -0.44 - (-0.28) = \boxed{-}0.16\ V$$

non-spntanuse

If $[Co^{+2}] = 0.25M$, $[Fe^{+2}] = 0.94\ M$

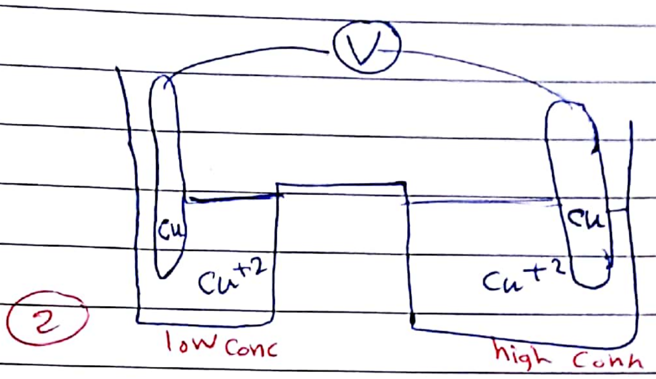
calc E_{cell}

25 C° => 298.

$$E = -0.16 - \frac{8.314 \times \boxed{298}}{2 \times 96485} \ln \frac{0.25}{0.94}$$

$E = -0.14$.

* اذا طلب حساب: (K) نحسبها فقط من E°



⇒ تحصل الاعادة
بسبب التراكيز .
فالمحلولات لازالة
تصبح تفاعل .

①

$$Cu^{+2} + 2e^- \rightarrow Cu + \quad E^\circ\ 0.34$$

$$Cu^{+2} + 2e^- \rightarrow Cu_{(s)} \quad 0.34$$

$$E^\circ = 0.34 - 0.34 = \underline{\underline{Zero}}. \leftarrow$$

في حالة الظروف العيارية لا يوجد
تيار .

②

low con.	high conc.
oxidation	reduction.
anode	cathode.

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = 0 - \frac{RT}{2F} \ln \frac{low}{high} \Rightarrow$$

* لكن تكون قيمة النسبة
سالبة $\ln \frac{low}{high}$
فالسالبة يلي بالقانون
تصبح اشارة (E) موجبة
اذا سيكون التفاعل تلقائي وهو كذلك .

Electrolysis. التحليل الكهربائي .

① $NaCl_{(l)}$ ② $H_2O_{(l)}$ ③ $NaCl_{(aq)}$

① $NaCl_{(l)}$

$$NaCl_{(s)} \xrightarrow{heat} Na^+_{(l)} + Cl^-_{(l)}$$

Two rxn :

$Na^+ + e \rightarrow Na_{(s)}$ (reduction)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (oxidation)

$Na^+ + e^- \rightarrow Na$ $-2.71\,V$ anode

$2Cl^- \rightarrow Cl_2 + 2e^-$ $+1.36\,V$ cathode.

$E^\circ cell = 1.36 - (-2.71) = 4.07\ V$

∝ to electrlys NaCl (l) 4.07 V must be applied to have the rxn to go. يعني اذا لتشغل بدو يصير بالعكس .

② electrolysis of H_2O

over all rxn $2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)}$

anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^\circ = 1.23$ V الأكسدة

cathode $H^+ + e \rightarrow \frac{1}{2} H_2$ $E^\circ =$ zero الاختزال

$E^\circ cell = -1.23$

عند زيد تركيز ايونات (H^+) في الماء

③ electrolysis of NaCl solution

Two oxidation rxn

$2Cl^- \rightarrow Cl_2 + 2e^-$ E°_{red} 1.36 V

$2H_2O \rightarrow \underbrace{O_{2(g)}}_{} + 4H^+ + 4e^-$ $E^\circ_{red} = 1.23$ V

عملياً ما بطلع O_2

بطلع بداله Cl_2 لأن

less positive لأن التفاعل أكسدة مو اختزال.

Theoretically this rxn will occur.

Three reduction rxn

$2H^+ + 2e^- \rightarrow H_{2(g)}$ $E^\circ =$ zero ①

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\circ = -0.83$ ②

$Na^+ + e^- \rightarrow Na_{(s)}$ $E^\circ = -2.71$ ③

بالتجربة التفاعل الثاني هو الذي يحدث.

* $V = \underbrace{I}_{\text{التيار}} \underbrace{R}_{\text{المقاومة}}$

* charge passed = current × time

(C) بوحدة الكولوم A أمبير × second.

* number of electrons = $\frac{\text{charge passed}}{\text{charge one } e^-}$

* charge of 1 mole of e^- = $6.022 \times 10^{23} \times 1.6 \times 10^{-19}$ C

= $\boxed{96485 \text{ C/mol}}$

مهم

→ Faraday constant.

* number of mol of e^- = ~~nF~~ $\frac{\text{charged passed}}{F} = \frac{\text{current} \cdot t}{F}$

Example : electrolysis of $CaCl_2$ (l).

How ~~much~~ many grams of Cl_2 produced if current = 0.452 A , time = 1.5 hour

Solution :-

$CaCl_2 \rightarrow Ca^{2+}_{(s)} + 2Cl^-_{(g)}$

$2Cl^- \rightarrow Cl_2 + 2e^-$

تحويل للثواني

moles of e^- = $\frac{0.452 \times \overbrace{1.5 \times 60 \times 60}}{96485}$ = 0.0253 mol

moles Cl_2 = $\frac{0.0253}{2}$ = 0.0126 mol

من النسبة من المعادلة الموزونة .

mass of Cl_2 = 0.0126 × 71 = 0.896 g

كتلة Cl_2

موجب $\boxed{Cl}$

② How much time is need to produce 7.0 g of $Cl_2(g)$.

Solution.

moles of $Cl_2 = \frac{1}{71} = 0.014$ mol

moles of $e^- = 0.14 \times 2 = 0.028$ mol

$$0.028 = \frac{0.452 \times time}{96485}.$$

time = 5976.9 Sec = 1.6 hr