

## A common exam question

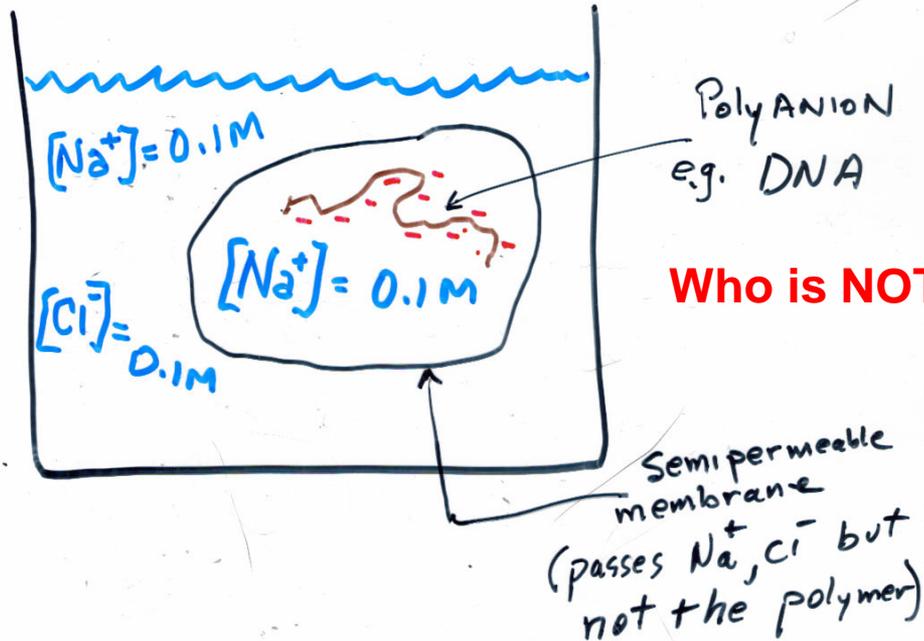
If  $\Delta\mu = +11.4 \text{ kJ/mol}$  for moving  $\text{Na}^+$  from in  $\rightarrow$  out

What is  $\Delta G$  to move 2 moles of  $\text{Na}^+$  from in  $\rightarrow$  out ?  
(remember that  $\Delta\mu$  is just  $\Delta G$  for 1 mol

Answer:  $2 \text{ mol} * 11.4 \text{ kJ/mol} = 22.8 \text{ kJ}$

# DONNEN MEMBRANE POTENTIAL

NaDNA =  
Sodium salt  
of DNA which  
is a very poly-protic  
acid.



Initially: charge balanced  $\Phi_{in} = \Phi_{out}$   
 $\text{Na}^+$  is at equilibrium

$$\mu_{\text{Na}^+_{in}} = \mu_{\text{Na}^+_{out}}$$

but  $\text{Cl}^-$  is NOT at equilibrium

$\text{Cl}^-_{out} \rightarrow \text{Cl}^-_{in}$  very spontaneous

$$\Delta\mu_{\text{Cl}^-} = \Delta\mu^{\circ}_{\text{Cl}^-} + 5.7 \log \frac{[\text{Cl}^-]_{in}}{[\text{Cl}^-]_{out}} + (-1)F(\Phi_{in} - \Phi_{out})$$

Equl:  $0 = 0 + 5.7 \log \frac{x}{.1} - F \Delta\Phi$

$x = ([\text{Cl}^-]_{in})_{eq}$

$x = [\text{Cl}^-]$  is small

$\Delta\Phi$  negative inside

What else happens? Is this really equilibrium?

## EQUILIBRIUM IS REACHED

When negative  $\Delta G$  from  $RT \ln \frac{[Cl^-]_{in}}{[Cl^-]_{out}}$

balances positive  $\Delta G$  from

Similarly for  $Na^+$ :

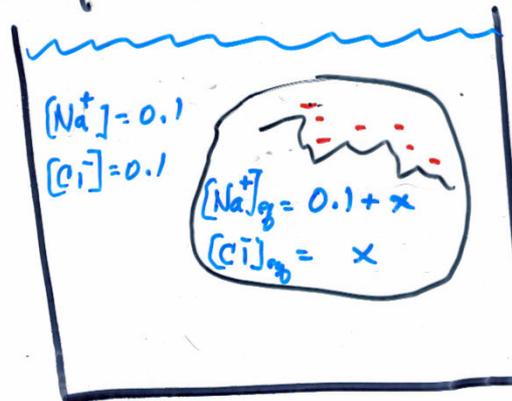
$$(-1)F(\phi_{in} - \phi_{out})$$

negative.

$Na^+$  follows  $Cl^-$  in

Outside is kept at 0.1 M

At Equilibrium:



Charge is NOMINALLY BALANCED  
 $\sim 10^{-14}$  mol more  $Cl^-$  than  $Na^+$   
 creates the Voltage difference

$$Na^+ \quad 5.7 \log \frac{0.1+x}{.1} + (1)F \Delta\phi = 0$$

$$Cl^- \quad 5.7 \log \left( \frac{x}{.1} \right) + (-1)F \Delta\phi = 0$$

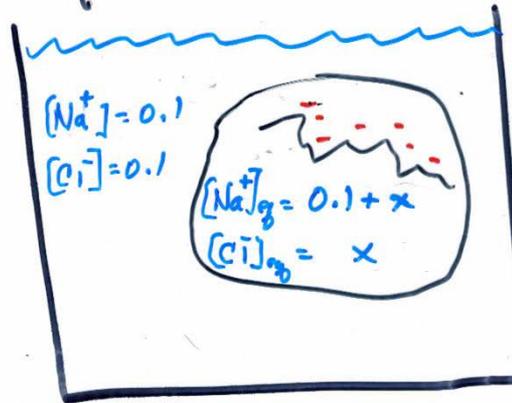
Solved by  $x = 0.0618M$

$$\Delta\phi = \frac{-5.7}{F} \log \left( \frac{0.1618}{0.1} \right) = -0.0592 \log(1.62)$$

$$= -0.012 \text{ Volts}$$

**-12 mV**

At Equilibrium :



Charge is  
NOMINALLY BALANCED  
 $\sim 10^{-14}$  mol more  
 $\text{Cl}^-$  than  $\text{Na}^+$   
Creates the  
Voltage difference

$$\text{Na}^+ \quad 5.7 \log \frac{0.1+x}{.1} + (1) F \Delta\phi = 0$$

$$\text{Cl}^- \quad 5.7 \log \left( \frac{x}{.1} \right) + (-1) F \Delta\phi = 0$$

Solved by  $x = 0.0618 \text{ M}$

$$\Delta\phi = \frac{-5.7}{F} \log \left( \frac{0.1618}{0.1} \right) = -0.0592 \log(1.62) = -0.012 \text{ Volts}$$

-12 mV

Outside is kept at 0.1 M

$$\frac{0.1+x}{0.1} = \frac{0.1}{x}$$

$$x^2 + 0.1x = 0.01$$

**quadratic equation** :  $x^2 + 0.1x - 0.01 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2} = \frac{-0.1 \pm \sqrt{0.01 + 0.04}}{2} = 0.0618 \text{ or } -0.1618$$

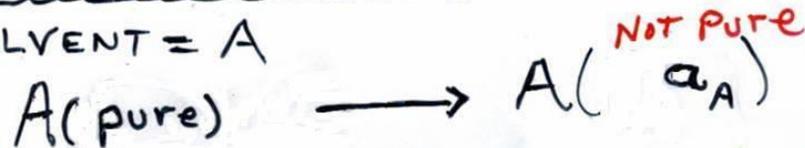
# COLLIGATIVE PROPERTIES

Properties of LIQUID OR SOLID that depend ONLY on  $X_{\text{SOLID}}$  or  $X_{\text{LIQUID}}$

i.e. ON MOLES OF SOLUTE

Not the identity of solute

SOLVENT = A



$a_A = \text{activity in solution} = \gamma_A X_A = \text{less than } 1$

$$\Delta \mu_A = \Delta \bar{G}_A = \Delta \bar{G}^\circ + RT \ln \frac{a_A}{1}$$

Osmotic Pressure.  $A(l, \text{pure}) \longrightarrow A(l, X_A < 1)$

Melting Point Depression  $A(s, \text{pure}) \longrightarrow A(l, X_A < 1)$

Boiling Point Elevation  $A(l, X_A < 1) \longrightarrow A(\text{gas})$

Vapor Pressure Depression " "

## Mole Fractions

Note: A could be liquid **or solid** (there are solid solutions)

At LOW solute concentration solution is ideal, so  $a_A = X_A < 1$

A powerful force

Anti-freeze, salt on roads

**This is why boiling point is raised**

What do the following 4 processes have in common?

**A(liq,  $X_A=1$ )  $\rightleftharpoons$  A(solid,  $X_A=1$ ) at melting point**

**A(liq,  $X_A=1$ )  $\rightleftharpoons$  A(gas,  $P_A=\text{vap press}$ ) at any T**

**A(liq,  $X_A=1$ )  $\rightleftharpoons$  A(gas,  $P_A=1$ ) at boiling point**

**A(liq,  $X_A=1$ )  $\rightleftharpoons$  A(liq,  $X_A=1$ ) at any T**

**ALL at equilibrium**

**i.e., ALL have  $\Delta G = 0$**

**which have  $\Delta G^0 = 0$ , i.e.,  $K = 1$ ?**

**all except 2<sup>nd</sup> have  $\Delta G^0 = 0$**

What do the following 4 processes have in common?

**A(liq,  $a_A < 1$ )  $\rightarrow$  A(solid,  $X_A=1$ ) at melting point**

**A(liq,  $a_A < 1$ )  $\rightarrow$  A(gas,  $P_A = \text{vap press}$ ) at any T**

**A(liq,  $a_A < 1$ )  $\rightarrow$  A(gas,  $P_A = 1$ ) at boiling point**

**A(liq,  $a_A < 1$ )  $\rightarrow$  A(liq,  $X_A = 1$ ) at any T**

**ALL spontaneous left**

**i.e., ALL have  $\Delta G = +$**

**which have  $\Delta G^0 = 0$ , i.e.,  $K = 1$ ?**

**all have  $\Delta G^0 = 0$ , except 2<sup>nd</sup>**

**same answer: changing conc. does not change  $\Delta G^0$**



$$Q = X_{\text{H}_2\text{O}}(\text{liq})/X_{\text{H}_2\text{O}}(\text{s}) \text{ if ideal}$$

*(when  $\gamma=1$ , it is ideal)*

$$\Delta G = \Delta G^0_{273} + RT \ln(Q/Q^0)$$

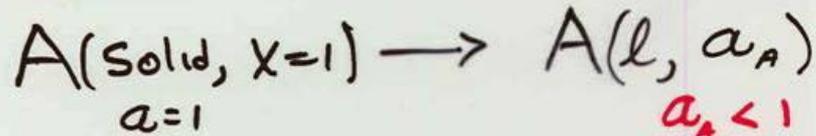
At melting point for pure solid and liquid:

**Equilibrium**

$$\Delta G = 0, (Q/Q^0)_{\text{eq}} = 1/1, K = 1$$

$$\Delta G^0_{273} = 0$$

# MELTING POINT LOWERING



What does LeChatelier say about this?

$$\Delta G_{\text{fus}} = \bar{\Delta G}_{\text{fus}}^{\circ} + RT \ln \left( \frac{a}{1} \right)$$

What is the equation for  $\Delta G_{\text{fusion}}$ ?

At melting point  $\Delta G = 0 \therefore \bar{\Delta G}_{\text{fus}}^{\circ} = -RT \ln a_g$   
(equilibrium)

What is required to get to equilibrium i.e.,  $\Delta G_{\text{fusion}} = 0$ ?

so  $K_{eq} = a_g$  given directly by  $\Pi$

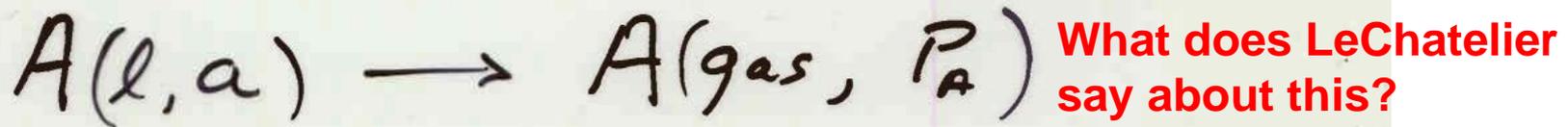
$\ln a_g$  is negative so  $\Delta G^{\circ} = +$

$$\ln \frac{K_m}{K_{273}} = \frac{-\Delta H^{\circ}}{R} \left( \frac{1}{T_m} - \frac{1}{273} \right) \text{ for H}_2\text{O}$$

$\ominus \quad \ominus \quad \oplus \therefore T_m < 273$   
lowering.

Solve for  $T_m$

# BOILING POINT RAISING



$$K_{\text{eq}} = \left( \frac{P_A}{a_{A(l)}} \right)_{\text{eq}}$$

what is equation for  $K_{\text{vap}}$ ?

For normal B.P.  $P_A = 1$

$$\ln \frac{K_{\text{b.p.}}}{K_{373}} = \ln \frac{1}{a} = -\frac{\Delta H_{\text{vap}}^{\circ}}{R} \left( \frac{1}{T_{\text{bp}}} - \frac{1}{373} \right)$$

$a < 1$

(+)

(-)

(-)

$T_{\text{bp}} > 373$

solve for  $T_{\text{b.p.}}$