

## Equations and Sample Problems

### Work

$$\text{work} = \text{force} \times \text{displacement} = f \times \Delta x = P \times A \times \Delta x = P \times \Delta V$$

where P = pressure, A = area, V = volume

The concept of PΔV work helps us understand function and energy requirements of lung, heart

We can also apply the concept to chemical work of cells and tissues.

$$\text{Chemical work} = \pi \Delta V = \pi \Delta(n/C) = CRT n \Delta C/C = RT n \log_e C/C' = 2.3 RT n \log_{10} C/C'$$

where π = osmotic pressure and n = number of moles

### Osmotic Pressure

$$\pi = C R T$$

where C is in moles/L

R = 62.3 L (mmHg) moles<sup>-1</sup> deg<sup>-1</sup> = molar gas constant

T = deg (absolute scale) = 273° + °C

Problem: Calculate π (in mm Hg) at 37°C for a 5% glucose (M.W. 180) solution.

5% glucose (M.W. 180) is 5g/100ml = 50g/l = (50/180) moles/l = 0.28 moles/l.

$$\begin{aligned} \pi &= C R T \\ &= 0.28 \text{ moles/l} \times 62.3 \text{ L (mmHg) moles}^{-1} \text{ deg}^{-1} \times 310 \text{ deg} \\ &= 5408 \text{ mmHg} \end{aligned}$$

Problem: Use the equation **work = 2.3 CRT C n C log C/C'**

to calculate the chemical work of parietal secretion for the following example

	[H <sup>+</sup> ]	[Cl <sup>-</sup> ]	[K <sup>+</sup> ]
parietal secretion (C)	.159M	.166M	.0074M
blood plasma (C')	4 × 10 <sup>-8</sup> M	.105M	.0047M

	C	C'	C/C'	log C/C'	n (moles)	n C log C/C'
[H <sup>+</sup> ]	.159M	4 × 10 <sup>-8</sup> M	3.98 × 10 <sup>6</sup>	6.599	.159	1.049
[Cl <sup>-</sup> ]	.166M	.105M	1.581	.199	.166	.033
[K <sup>+</sup> ]	.0074M	.0047M	1.574	.197	.0074	<u>.015</u>

Sum = 1.097 moles

$$\begin{aligned} \text{work} &= 2.3 CRT C n C \log C/C' \\ &= 2.3 (1.98 \text{ cal/mole/deg}) (310 \text{ deg}) (\text{sum}) \\ &= 1549 \text{ cal} \end{aligned}$$

## Starling Hypothesis

Hydrostatic and osmotic pressures control the flow of solvent across a semi-permeable membrane, and account for fluid exchange across capillaries. The flow depends on the filtration pressure ( $\Delta P - \Delta\pi$ ), where  $\Delta P$  = difference of hydrostatic pressure and

$\Delta\pi$  = difference of osmotic pressure

In a capillary the pressures are approximately

<u>Arteriole</u>	$\Delta P = 40 \text{ mmHg}$	$\Delta P = 10 \text{ mmHg}$	<u>Venule</u>
	$\Delta\pi = 25 \text{ mmHg}$	$\Delta\pi = 25 \text{ mmHg}$	
fluid out $\dot{u}$	_____	_____	fluid in $\dot{u}$
	$\Delta P - \Delta\pi = 15 \text{ mmHg}$	$\Delta P - \Delta\pi = -15 \text{ mmHg}$	

Problem: In a capillary, the net hydrostatic pressure is 40 mm Hg and the net osmotic pressure is 15 mmHg. Calculate the filtration pressure (F.P.).

$$\begin{aligned} \text{filtration pressure} &= \Delta P - \Delta\pi \\ &= 40 \text{ mmHg} - 15 \text{ mmHg} \\ &= 25 \text{ mmHg} \end{aligned}$$

What happens to the filtration pressure if 1 mmole of an impermeant neutral polymer is added per liter of plasma?

Calculate the additional osmotic pressure, add it to  $\Delta\pi$  and subtract from  $\Delta P$ .

## pH Equilibria

$$\begin{aligned} \text{HA} &\rightleftharpoons \text{H}^+ + \text{A}^- & K &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \\ \log K &= \log \frac{[\text{A}^-]}{[\text{HA}]} + \log \text{H}^+ \\ \text{pH} &= \text{pK} + \log \frac{[\text{A}^-]}{[\text{HA}]} \end{aligned}$$

Problem: A 24 hour sample of urine contains 4.5g of phosphate ( $\text{H}_2\text{PO}_4^{-1} + \text{HPO}_4^{-2}$ ) per liter. The pH of the urine is 6.21, while the body pH is 7.4. Calculate the amount of cation saved by the kidney through substitution of  $\text{H}^+$ .

<i>Urine</i>	<i>Body</i>
$6.21 = 7.198 + \log \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]}$	$7.4 = 7.198 + \log \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]}$
$\log \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]} = 0.988$	$\log \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]} = .202$
$\frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]} = 0.102$	$\frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-1}]} = 1.592$

$$\begin{array}{ll} \frac{[\text{H}_2\text{PO}_4^{-1}]}{[\text{HPO}_4^{-2}] = x} & \frac{[\text{H}_2\text{PO}_4^{-1}]}{[\text{H}_2\text{PO}_4^{-1}] = 0.102x} \\ \text{If } [\text{HPO}_4^{-2}] = x & \text{If } [\text{HPO}_4^{-2}] = x \end{array} \quad \frac{[\text{H}_2\text{PO}_4^{-1}]}{[\text{H}_2\text{PO}_4^{-1}] = 1.592x}$$

Since the total phosphate ( $\text{H}_2\text{PO}_4^{-1} + \text{HPO}_4^{-2}$ ) in both cases is 4.5g/l

$$\begin{array}{ll} \text{Urine} & \text{Body} \\ x \text{ C96 g/mole} + 0.102x \text{ C97 g/mole} = 4.5 \text{ g} & x \text{ C96 g/mole} + 0.102x \text{ C97 g/mole} = 4.5 \text{ g} \\ x = .0421 \text{ moles } \text{H}_2\text{PO}_4^{-1} & x = .018 \text{ moles } \text{H}_2\text{PO}_4^{-1} \end{array}$$

$$.0421 \text{ moles } \text{H}_2\text{PO}_4^{-1} - .018 \text{ moles } \text{H}_2\text{PO}_4^{-1} = .0241 \text{ cation replaced by } \text{H}^+$$

## Nernst Equation

Differences in chemical potential are due to differences in concentration. The difference in chemical potential can be measured as an electrical potential when it is expressed across a membrane or an electrode surface. The difference in electrical potential in millivolts at 20°C

$$\Delta E = 58 \log_{10} \frac{C_1}{C_2}$$

where  $C_1$  and  $C_2$  are concentrations in the same units.

Problem: Calculate the electrical potential difference (and give its direction) for the following case:

Solution I contains 100 mMol/L KCl and Solution II contains 10 mMol/L KCl.

The membrane between I and II is permeable to  $\text{K}^+$  only.

$$\Delta E = 58 \log_{10} \frac{C_1}{C_2} = 58 \log_{10} \frac{100}{10} = 58 \log_{10} 10 = 58 \text{ mV}$$

The direction of the electrical potential difference is determined by seeing which way the ion flux will charge up the membrane. K ions flow from I to II making side II more positive and impeding the further flow of K ions.

## Electron transfer

Because electron transfer is driven by differences in chemical potential, equilibria involving electrons are governed by an equation similar to the Nernst equation. For the reaction

$$E = E^0 + 2.3 \frac{RT}{F} \log_{10} \frac{[\text{ox}]}{[\text{red}]} = E^0 + 2.3 \frac{RT}{F} \log_{10} \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]}$$

where  $E^0$  has a different value for each reaction.

Problem: Mix two Fe containing solutions together, and see how they equilibrate.

Mix: 10ml 0.1M  $\text{FeCl}_3$  (this is in the ferri form)  $E^0 = .36\text{volts}$

10ml 0.1M  $K_4[Fe(CN)_6]$  (this is in the ferro form)  $E^0 = .771\text{volts}$

If we assume that  $x$  mmols of  $Fe^{+3}$  react to become  $Fe^{+2}$ , and the ferrocyanide changes to ferricyanide, then the 20ml mixture will have the following concentrations:

$Fe^{+3}$	$Fe^{+2}$	ferrocyanide	ferricyanide
$\frac{1\text{mmol}-x}{20\text{ml}}$	$\frac{x}{20\text{ml}}$	$\frac{1\text{mmol}-x}{20\text{ml}}$	$\frac{x}{20\text{ml}}$

At equilibrium, the E's will be equal.

$$E = .771 + .059 \log_{10} \frac{1-x}{x} = .36 + .059 \log_{10} \frac{x}{1-x}$$

$$.441 = .059 \log_{10} \frac{x}{1-x}^2$$

$$x = 0.999671 \text{ mmoles} \quad \text{and} \quad \frac{1-x}{20} = 1.645 \times 10^{-5} \text{ M}$$

$$E = .771 + .059 \log_{10} \frac{1-x}{x} = .771 + .059 \log_{10} \frac{1.645 \times 10^{-5}}{5 \times 10^{-2}}$$

$$E = .566\text{volts}$$

**Capacitance**,  $C$ , relates the charge to the potential

$$Q = C V, \quad \text{where } Q = \text{charge and } V = \text{potential}$$

Problem: Calculate the charge at the membrane surface when the membrane potential is 100mV.

$$\begin{aligned} Q &= C V \\ &= 10^{-6} \text{ farads/cm}^2 \times 0.1 \text{ volt} \\ &= 10^{-7} \text{ coul/cm}^2 \quad (\text{farad} = \text{coul/volt}) \\ &= 10^{-12} \text{ equiv/cm}^2 = \text{pequiv/cm}^2 \quad (10^5 \text{ coul/equiv; the prefix p} = 10^{-12}) \\ Q &= 6 \times 10^{11} \text{ ions/cm}^2 \quad (6 \times 10^{23} \text{ ions/equiv}) \end{aligned}$$

Keep in mind that the ion fluxes during action potentials are measured in picomoles/cm<sup>2</sup>

### Ohm's Law

For all conductors, including ionic solutions,  $I$ , the current (charges per unit time)

$$I = \frac{\Delta E}{R} \quad \begin{aligned} \Delta E &= \text{difference of electrical potential} \\ R &= \text{electrical resistance} \\ G &= 1/R_e = \text{electrical conductance} \end{aligned}$$

Ions move with different mobilities, given in units of  $\frac{\text{cm/sec}}{\text{volt/cm}}$

$$H^+ \quad 36.2 \times 10^{-4}$$

$$\begin{aligned} \text{Na}^+ & 5.2 \times 10^{-4} \\ \text{K}^+ & 7.6 \times 10^{-4} \\ \text{Cl}^- & 7.9 \times 10^{-4} \end{aligned}$$

## Chord Conductance Equation

$$E_M = \frac{g_K}{\Sigma g} E_K + \frac{g_{Na}}{\Sigma g} E_{Na} + \frac{g_{Cl}}{\Sigma g} E_{Cl}$$

where  $g$  is ionic conductance and  $E$  is the chemical potential difference in electrical units.

Problem: Solve problem 6 page 29 in text by direct substitution in the above equation.

## Gibbs-Donnan Equilibrium

is characterized by a semi-permeable membrane and charged osmotically active ion

- |  |     |                 |                 |                                |
|--|-----|-----------------|-----------------|--------------------------------|
| (1) Initial conditions<br>(equal concentrations)   | (1) | 5               | (2)             |                                |
| (2) Imbalance leads to ion flow<br>(Na <sup>+</sup> , Cl <sup>-</sup> both move 1° 2)                    |     | Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> R <sup>-</sup> |
| (3) Equilibrium (chemical and<br>electrical potentials balance)<br>Charging due to ion fluxes creates ΔE |     | Na <sup>+</sup> | +5»             | Na <sup>+</sup>                |
|  |     | Cl <sup>-</sup> | ° 5-            | Cl <sup>-</sup>                |
|  |     |                 | + 5 -           |                                |

Equating chemical and electrical potentials,

$$\text{For Na}^+ \quad \mu_{Na}^{\circ} + RT \ln [Na_1] = \mu_{Na}^{\circ} + RT \ln [Na_2] - F \Delta E_m$$

$$\text{For Cl}^- \quad \mu_{Cl}^{\circ} + RT \ln [Cl_1] = \mu_{Cl}^{\circ} + RT \ln [Cl_2] + F \Delta E_m$$

$$\text{Adding the equations:} \quad RT \ln [Na_1] [Cl_1] = RT \ln [Na_2] [Cl_2]$$

$$\text{Equilibrium condition:} \quad [Na_1] [Cl_1] = [Na_2] [Cl_2]$$

$$\text{Donnan Ratio:} \quad r = \frac{[Na_1]}{[Na_2]} = \frac{[Cl_2]}{[Cl_1]}$$

$$\text{Membrane Potential:} \quad \Delta E = 58 \log_{10} \frac{[Na_1]}{[Na_2]} = 58 \log_{10} \frac{[Cl_2]}{[Cl_1]}$$

$$\begin{aligned} \text{Osmotic Pressure:} \quad \pi &= (C_p + C_e) RT \\ C_p &= \text{impermeable ion} \\ C_e &= \text{excess salt } (Na_2 + Cl_2) - (Na_1 + Cl_1) \end{aligned}$$

Problem: For a Gibbs-Donnan Equilibrium, the initial concentrations are solution I, 3mMol/L NaCl and solution II, 3 mMol/L NaP. (The membrane is impermeable to P<sup>-</sup>.) Assume equal volumes, and that the pressure necessary for osmotic equilibrium is applied so there are not water fluxes. Calculate the following:

- The equilibrium concentrations of the ions
- The magnitude of the membrane potential and its direction.
- The hydrostatic pressure that has been applied to maintain osmotic equilibrium. (at 37°C)

Assume x = the number of moles that move from I to II

Equilibrium condition: 
$$\frac{[Na_1] C [C1_1]}{(3-x) (3-x)} = \frac{[Na_2] C [C1_2]}{(3+x) (x)}$$

$$x = 1$$

Concentrations are: 
$$\frac{[Na_1] C [C1_1]}{2M \quad 2M} = \frac{[Na_2] C [C1_2]}{4M \quad 1M}$$

Membrane Potential: 
$$\Delta E = 58 \log_{10} \frac{[Na_1]}{[Na_2]} = 58 \log_{10} \frac{[C1_2]}{[C1_1]}$$

$$\Delta E = 58 \log_{10} \frac{2}{4} = 58 \log_{10} \frac{1}{2} = 17.5 \text{ mV}$$

Osmotic Pressure: 
$$\pi = \{[Na_2] + [C1_2] + [R]\} - \{[Na_1] + [C1_1]\} R CT$$

$$= \{ 4 + 1 + 3 \} - \{ 2 + 2 \} R CT$$

$$= .004Mol/l \quad R CT$$

$$= 77.25\text{mmHg}$$