

# LEARNING PREREQUISITES - DILUTE SOLUTION

Important: These handouts give a brief overview of the prerequisites for this chapter («dilute solution» )  
For further reading, see : P.W. Atkins, Physical Chemistry

Three principles governing the relationships between different forms of energy.

The **first law of thermodynamics** (law of conservation of energy) states that the change in the internal energy of a system is equal to the sum of the heat added to the system and the work done on it.

Or in other words: Energy cannot be created or destroyed, only transformed

$$\Delta U = q + w$$

The **second law of thermodynamics** states that heat cannot be transferred from a colder to a hotter body within a system without net changes occurring in other bodies within that system; in any irreversible process, entropy always increases.

$$\Delta S_{\text{tot}} > 0$$

The **third law of thermodynamics** (Nernst heat theorem) states that it is impossible to reduce the temperature of a system to absolute zero in a finite number of steps

(General Physics) Also called: **zeroth law of thermodynamics** the principle that if two bodies are each in thermal equilibrium with a third body then the first two bodies are in thermal equilibrium with each other

State functions = properties that are independent of how the sample was prepared.

## Fundamental Equations and Maxwell Relations

$$dU = TdS - pdV$$

**Enthalpy:**

$$H = U + pV$$

$$dH = TdS + Vdp$$

**Helmholtz energy:**

$$A = U - TS$$

$$dA = -SdT - pdV$$

**Gibbs energy:**

$$G = H - TS$$

$$dG = -SdT + Vdp$$

**Table 3.5** The Maxwell relations

From  $U$ :  $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

From  $H$ :  $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

From  $A$ :  $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

From  $G$ :  $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Table 3-5  
Atkins Physical Chemistry, Eighth Edition  
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The fundamental equations combines the First and the Second Laws.

*Fundamental thermodynamic functions for closed systems*

name	definition	differential form	natural variables	conditions at equilibrium
internal energy		$dU = TdS - PdV$	$U(S, V)$	minimized at constant $S$ and $V$
enthalpy	$H \equiv U + PV$	$dH = d(U + PV)$ $= dU + PdV + VdP$ $= TdS + VdP$	$H(S, P)$	minimized at constant $S$ and $P$
Helmholtz free energy	$A \equiv U - TS$	$dA = d(U - TS)$ $= dU - TdS - SdT$ $= -SdT - PdV$	$A(T, V)$	minimized at constant $T$ and $V$
Gibbs free energy	$G \equiv U + PV - TS$ $= A + PV$ $= H - TS$	$dG = d(H - TS)$ $= dH - TdS - SdT$ $= -SdT + VdP$	$G(T, P)$	minimized at constant $T$ and $P$

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy.

**Enthalpy ( $H$ )** is the sum of the internal energy ( $U$ ) and the product of pressure and volume ( $PV$ ) given by the equation:

$$H = U + PV$$

Also at constant pressure the heat flow ( $q$ ) for the process is equal to the change in enthalpy defined by the equation:  $\Delta H = q$   
energy measures the capability of an object or system to do work.

**Entropy**, on the other hand, is a measure of the "disorder" of a system. What "disorder" refers to is really the number of different microscopic states a system can be in, given that the system has a particular fixed composition, volume, energy, pressure, and temperature. By "microscopic states", we mean the exact states of all the molecules making up the system.

Statistical definition of entropy: calculating the degree of disorder in a system using a formula proposed by L. Boltzmann:  $S = k \ln \Omega$   
with Boltzmann's constant  $k = 1,381 \times 10^{-23} \text{ J/K}$  and  $\Omega$  = number of different ways in which the energy of the system can be achieved

Thermodynamic equation for the **Gibbs energy** change accompanying mixing at constant temperature and pressure is

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

# Osmotic Pressure – Van't Hoff Equation

At equilibrium the chemical potential of the pure solvent is equal to the chemical potential of the solution, which is under an applied osmotic pressure,  $\Pi$  (= applied pressure  $P$  – atmospheric pressure 1), i.e.

$$\mu_A^\circ (\text{pure solvent}) = \mu_A^P (\text{solvent in solution under pressure, } P) \quad (\text{O1})$$

For the pure solvent, since  $dG \equiv d\mu = VdP - SdT$

we can write, for constant temperature,

$$\int_{\mu_A^\circ}^{\mu_A^P} d\mu_A^\circ = \int_{P=1}^P V_A dP$$

which leads to

$$\mu_A^P = \mu_A^\circ + (P - 1)V_A = \mu_A^\circ + \Pi V_A$$

For the chemical potential of the solvent in an ideal solution, we must add the contribution of the free energy of mixing. When we substitute the result into equation (O1) we obtain

$$\mu_A^\circ = \mu_A^\circ + \Pi V_A + RT \ln x_A$$

Hence

$$\Pi V_A = -RT \ln x_A = -RT \ln(1 - x_B) \approx RT x_B$$

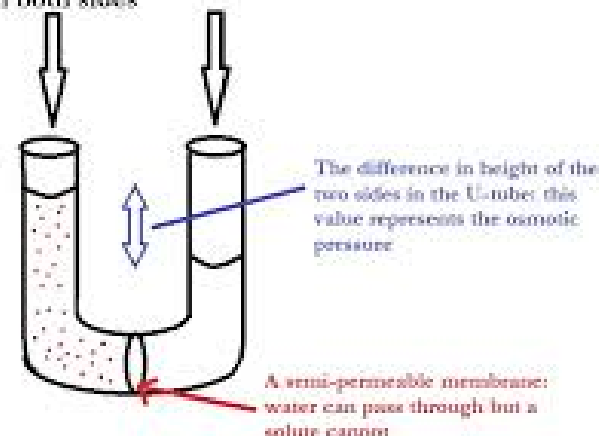
If  $c_B$  is the concentration in  $\text{g dm}^{-3}$  we can write

$$\frac{x_B}{V_A} \approx \frac{c_B / M_B}{1000 \rho_A / M_A} \times \frac{1000 \rho_A}{M_A} = \frac{c}{M_B}$$

Hence

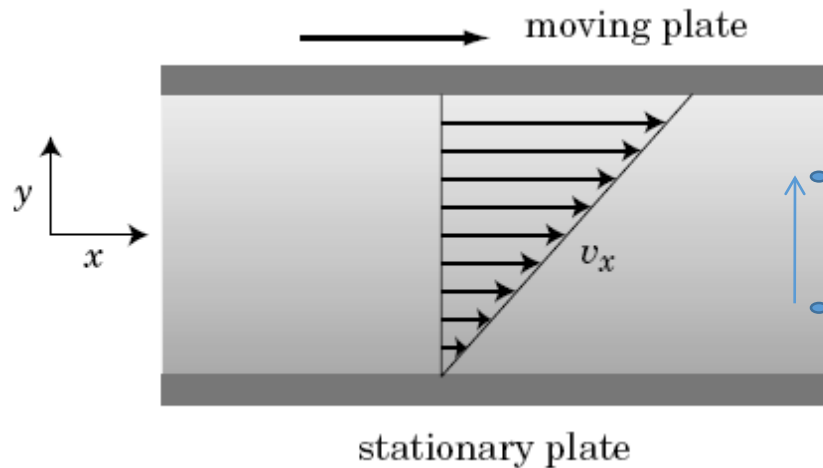
$$\frac{\Pi}{c_B} = \frac{RT}{M_B} \quad (\text{O2})$$

The pressure of the atmosphere is the same on both sides



# Viscosity

Viscosity is the transport of momentum along a velocity gradient  
 or Viscosity of liquids is the ratio of the applied shear stress to the resulting strain rate



**Viscosity** is the mechanical friction between molecules in motion, and the resistance to deformation because of mutual attraction of the molecules (in other words, resistance to flow).

There are two types of viscosity.

**Dynamic viscosity**, also known as **absolute viscosity**, is the tangential force per unit area required to move one horizontal plane with respect to another horizontal plane at a unit velocity when maintained a unit distance apart by the fluid.

**Kinematic viscosity** is the ratio of absolute/dynamic viscosity to density.

$$\eta \frac{\delta v_x}{\delta y} = \sigma_{yx}$$

shear stress  
 Newton's law  
 velocity gradient

$\eta$ : viscosity [Pa s] = 10 Poise, 1P = dyne s cm<sup>-2</sup>  
 $\dot{\gamma} = dv_x/dy$  strain rate

$\eta$ : measure for the resistance of the fluid to flow

The **Einstein equation of viscosity** is a description of how viscosity increases due to the presence of solid particles in a fluid. The specific viscosity  $\eta_{sp}$  is described in terms of the number  $n$ , and volume  $V$ , of the solid spheres suspended in unit volume of fluid with viscosity  $\eta_0$ .

$$\eta = \eta_0(1 + 2.5 nV)$$

or expressed with volume fraction  $v$ :  $\eta = \eta_0(1 + 2.5 v)$

The coefficient 2.5 has its origin in that the surface integral of the shear stress at the wall of the solid sphere is four times as great as the pressure drop across that sphere, and that the contribution to the overall viscosity from the pressure being equal to  $\eta_0/2$ .

Work in the semi-dilute regime has focused on finding coefficients for the higher order terms in  $v$  neglected by Einstein, producing relationships of the form:  $\eta_r = 1 + 2.5v + 4v^2 + \dots$

Consider a sphere falling through a viscous fluid. As the sphere falls so its velocity increases until it reaches a velocity known as the terminal velocity. At this velocity the frictional drag due to viscous forces is just balanced by the gravitational force and the velocity is constant (shown by Figure 2).

At this speed:

$$\text{Viscous drag} = 6\pi\eta rv = \text{Weight} = mg$$

The following formula can be proved (see dimensional proof)

$$\text{Frictional force } F = 6\pi\eta rv \quad \textbf{Stokes' law}$$

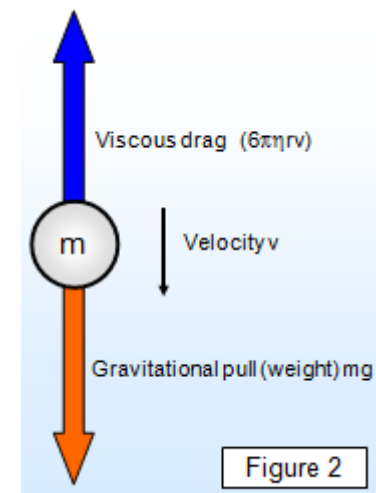
If the density of the material of the sphere is  $\rho$  and that of the liquid  $\sigma$ , then:

$$\text{Effective gravitational force} = \text{weight} - \text{upthrust} = \frac{4}{3}\pi r^3(\rho - \sigma)g$$

Therefore we have for the viscosity ( $\eta$ ):

$$\text{Viscosity } (\eta) = \frac{2gr^2(\rho - \sigma)}{9v}$$

**Hydrodynamic Volume**  $V_h$  is the volume of a [hydrodynamically equivalent sphere](#)  $V_h = \frac{vM}{cN_A}$



# Names and Definitions

Several methods exist for characterizing the capacity of the solute to increase the viscosity of the solution.

The most common solution viscosity terms are:

Symbol	Definition	Name
$\eta_{\text{rel}}$	$\frac{\eta}{\eta_s}$	Relative viscosity
$\eta_{\text{sp}} = \eta_{\text{rel}} - 1$	$\frac{\eta}{\eta_s} - 1$	Specific viscosity
$\eta_{\text{red}} = \eta_{\text{sp}}/c$	$\frac{1}{c} \left[ \frac{\eta}{\eta_s} - 1 \right]$	Reduced viscosity
$[\eta]$	$\lim_{c \rightarrow 0} \left[ \frac{\eta - \eta_s}{c \eta_s} \right]$	Intrinsic viscosity
$\eta_{\text{inh}}$	$\frac{1}{c} \ln \left[ \frac{\eta}{\eta_s} \right]$	Inherent viscosity

# Light Scattering

**Polarizability** is the ability to form instantaneous dipoles. It is a property of matter. Polarizabilities determine the dynamical response of a bound system to external fields, and provide insight into a molecule's internal structure. In a solid, polarizability is defined as the dipole moment per unit volume of the crystal cell

The polarizability  $\alpha$  in isotropic media is defined as the ratio of the induced dipole moment  $p$  of an atom to the electric field  $E$  that produces this dipole moment:  $p = \alpha E$

The induced dipole moment will radiate light in all directions  $\rightarrow$  light scattering occurs only in mediums that have an inhomogeneous index of refraction

$$\alpha_p = \frac{n_0 M}{2\pi N_A} \left( \frac{dn_0}{dc} \right) \quad n_0 \text{ refractive index of solution}$$

Refractive index  $n$  is the wavelength in the material  $\lambda$  relative to the wavelength in vacuum  $\lambda_0$  :  $n = \lambda/\lambda_0$