مناق الله العظم

سورة يوسف أيه 76



Basic Chemistry

for Engineering

State Of The Liquid Matter

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In the liquid state the forces of attraction among particles are great enough that disordered clustering occurs. The particles are so close together that very little of the volume occupied by a liquid is empty space. As a result, it is very hard to compress a liquid. Particles in liquids have sufficient energy of motion to overcome partially the attractive forces among them. They are able to slide past one another so that liquids assume the shapes of their containers up to the volume of the liquid.

Liquids diffuse into other liquids with which they are *miscible*. For example, when a drop of red food coloring is added to a glass of water, the water becomes red throughout after diffusion is complete. The natural diffusion rate is slow at normal temperatures. Because the average separations among particles in liquids are far less than those in gases, the densities of liquids are much higher than the densities of gases (Table 12-1).

Cooling a liquid lowers its molecular kinetic energy and causes its molecules to slow down even more. If the temperature is lowered sufficiently, at ordinary pressures, stronger but shorter-range attractive interactions overcome the reduced kinetic energies of the molecules to cause solidification. The temperature required for crystallization at a given pressure depends on the nature of short-range interactions among the particles and is characteristic of each substance.



The Characters of the liquid matter

- It has not constant shape.
- It has constant volume.
- It's ability to the compressibility and expansibility approximately = zero.
- The attraction forces are medium.
- Movement of the molecules is small.
- The distance between the molecules is small.
- Molecules arrangement is in groups.

Evaporation

"It can be defined as conversion of matter from the liquid form to the gas form "by heating process:

ex . Ether evaporation (Very Fast) while; Mercury evaporation (Very Slow), This is due to ; The high density of mercury (13 g/cc) than Ether (0.789 g/cc).

Explanation of the evaporation process by the molecular kinetic theory: "because of the randomize movement of liquid molecules, its velocity start to increase by absorbing heat, so the molecules reach to the container surface and start to leave it in gas form."



Evaporation

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Evaporation

is

The transformation of liquid into vapor

Latent heat of vaporization

Is the amount of heat energy required to cause evaporation of stated amount of liquid (either 1 gm or 1 mole).

Two conditions are necessary for a molecule to evaporate

- It must occupy a position at the surface.
- It must have kinetic energy in excess of a particular value.

The rate of evaporation

Is the number of molecules leaving the liquid surface per minute.

The rate of evaporation depends on:

- The amount of surface presented by the liquid.
- The fraction of molecules having kinetic energy in excess of the critical amount.

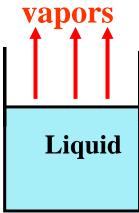
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2- Evaporation and cooling

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<u>Consider a liquid evaporating in an open vessel</u>

- Vapor molecules can diffuse into the atmosphere
- The more energetic molecules are lost by the liquid
- The average kinetic energy of the remaining molecules must decrease
- As heat is the kinetic energy of molecular motion the temperature of the liquid must therefore fall.



There is an attendant cooling effect accompanying evaporation

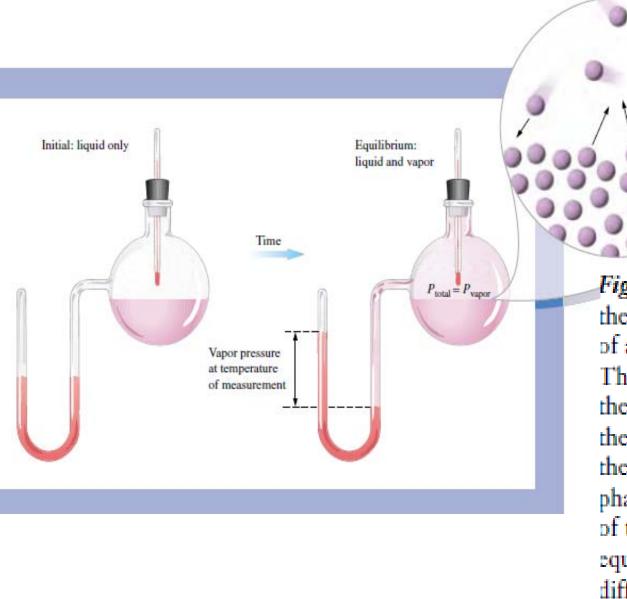


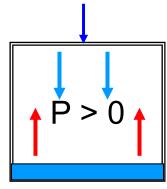
Figure 13-12 A representation of the measurement of vapor pressure of a liquid at a given temperature. The container is evacuated before the liquid is added. At the instant the liquid is added to the container, there are no molecules in the gas phase so the pressure is zero. Some of the liquid then vaporizes until equilibrium is established. The difference in heights of the mercury column is a measure of the vapor pressure of the liquid at that temperature.



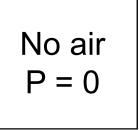
3- Evaporation in a closed container

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Closed Vessel

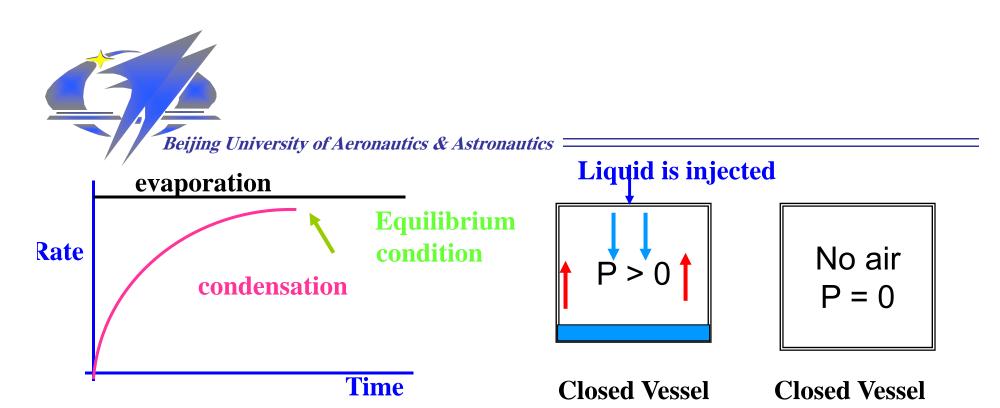


Closed Vessel

In a closed vessel, where molecules are not in position to leave the system completely, the condensation process can no longer be ignored.

As a result of evaporation the pressure will increase as more and more molecules enter the space above the liquid.

At any instant of time, some of the molecules will through collision be directed back to the liquid surface.



If a condition of constant temperature is exist, evaporation rate will proceed at constant rate.

As a result of evaporation the pressure will increase as more and more molecules enter the space above the liquid.

At any instant of time, some of the molecules will through collision be directed back to the liquid surface.

The condition of dynamic equilibrium is:

Rate of evaporation = rate of condensation

In this equilibrium state, the pressure exerted by the vapor is referred to as the vapor pressure

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Vapor pressure of liquids

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It is pressure of gas molecules when it will be in dynamic equilibrium with the liquid molecules"

* There is an irreversible relationship between the vapor pressure of liquids and the

temperature

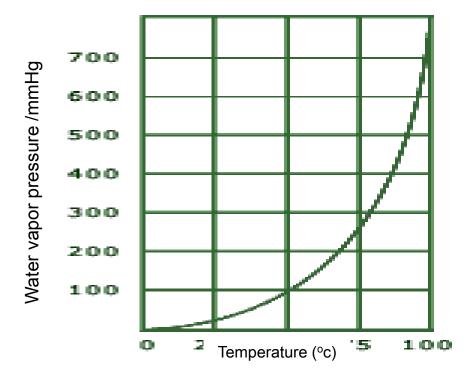


TABLE 11.4 Vapor Pressure of Water

5
9
18
32
47
55
93
149
234
355
528
760

^aBody temperature.

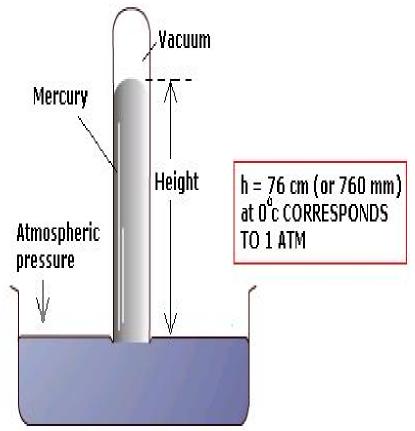
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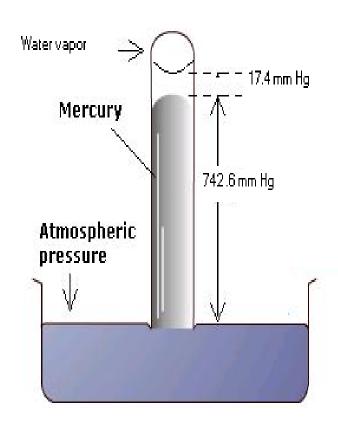


Measurement of liquids vapor pressure:

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The static's method (Barometer)





Measurement of liquid vapor pressure



Boiling point

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It occurs when the liquid vapor pressure (inside) = the atmospheric. pressure (outside)"

•If the atm. Pressure (outside) is low , the boiling point will decrease so the boiling point of water (H_2O) on the top of mountain is smaller than its value at the sea surface .

ex. Boiling point of
$$H_2O$$
 \longrightarrow 100 °C Liquid oxygen \longrightarrow - 183 °C .

IF The Liquid vapor pressure = 1 atm. (760 mm hg).

TABLE 11.4 Vapor Pressure of Water

Temperature (°C)	Vapor Pressure (mmHg)			
0	5			
10	9			
20	18			
30	32			
37^{a}	47			
40	55			
50	93			
60	149			
70	234			
80	355			
90	528			
100	760			

^aBody temperature.

TABLE 13-4	Vapor Pressures (in torr) of Some Liquids						
	0°C	25°C	50°C	75°C	100°C	125°C	
water	4.6	23.8	92.5	300	760	1741	
benzene	27.1	94.4	271	644	1360		
methyl alcohol	29.7	122	404	1126			
diethyl ether	185	470	1325	2680	4859		

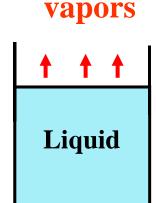
^{*} Standard boiling point (SBP).



4- Variation of vapor pressure with temperature: Boiling

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The fraction of molecules capable of leaving a liquid surface increases rapidly with temperature. The result is a rapid increase in the vapor pressure with increase with temperature.



Boiling Point

The temperature at which the vapor pressure of a liquid equals to the external pressure.

Normal boiling Point

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Is the boiling point when external pressure is 1 atm.



5- The Clapeyron Equation

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The quantitative relationship between vapor pressure and temperature is expressed by the clapeyron equation

$$dP / dT = L / T\Delta V$$

$$\Delta V = V_{vapour} - V_{liquid}$$

$$V_{vapour} >> V_{liquid}$$

$$\Delta V \approx V_{vapour}$$

$$V_{\text{vapour}} = \frac{RT}{P}$$
 for n = 1

vapors



Liquid

dp/dt: the rate at which the vapor pressure changes with temperature at T (K).

 \boldsymbol{L} : The latent heat of vaporization

 ΔV : the volume change from liquid into vapor



Derivation of the clapeyron equation

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$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

$$\frac{dP}{P} = \frac{L}{RT^2} dT$$

$$d \ln P = \frac{L}{RT^2} dT$$

$$\int_{P_1}^{P_2} d \ln P = \frac{L}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

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

$$\log \frac{P_2}{P_1} = \frac{L}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$



Example

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It is desired to produce superheated steam at 120°C, under what pressure must water be boiled to achieve this? Normal boiling point of water = 100°C. Latent heat of vaporization of water = 39.70 kJ mol⁻¹.

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Solution

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$$\because \log \frac{P_2}{P_1} = \frac{L}{2.303 \, R} \left(\frac{T_2 - T_1}{T_2 \, T_1} \right)$$

$$P_2 = ?$$
 , $P_1 = 1$ atm

$$T_2 = 120$$
°C = 393 K , $T_1 = 100$ °C = 373 K

 $L = 39.70 \text{ kJ mol}^{-1} = 39700 \text{ J mol}^{-1}$

$$\therefore \log \frac{P_2}{1} = \frac{39700 (393 - 373)}{2.303 \times 8.314 \times 393 \times 373}$$

- ∴ P_2 = 1.92 atm.
- ∴ Water must be boiled under a confining pressure of 1.92 atm. (autoclave or pressurized vessel)

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Freezing point

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"It can be defined as conversion of matter from the liquid state to the solid state by freezing process".

- * Explanation of the freezing process by the molecular kinetic theory:
- "When the temperature degree decrease, the kinetic energy of the liquid molecules will loss and its ability, to move, will loss too so the attraction forces will be increase and the molecules start to collect in crystalline form.
- * When the temperature degree of both solid state and liquid state is in dynamic equilibrium, this is call (freezing point) or (melting point). ex. Freezing point or melting point of water (H_2O) = Zero $^{\circ}C$ (32 $^{\circ}F$) at 1 atm.

Freezing point or melting point of liquid Hydrogen $(H_2) = -259$ °C at 1 atm.

* Standard Freezing or melting point (SFP) or (SMP):

It occurs when "the liquid state and the solid state has the same vapor pressure and the same atm. pressure (1 atm.),too.



Surface tension of liquids

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"It is the work (erg. cm⁻²) require for increase the surface area of liquid 1 cm²" Or " It is the force (dyne .cm -1) require for increase the liquid surface are" * Explanation of the surface tension phenomena "The molecules inside the liquid affected by the attraction forces (inside the liquid) this forces are equilibrium in all direction: But in the surface layer of the liquid, the attraction forces are not equilibrium in all directions, so the surface layer will be in tension state and affected by surface tension forces". Thus the liquids surfaces try to decreasing its area to decrease this surface tension (by taking the ball or the drop shape).

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Classification of liquids according to its surface tension

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I . High surface tension liquids

☑The attraction forces between the solid surface (capillary tube) and the liquid molecules are greater than the attraction forces between the liquid molecules. So; the liquid will be goes up as in the

figure.

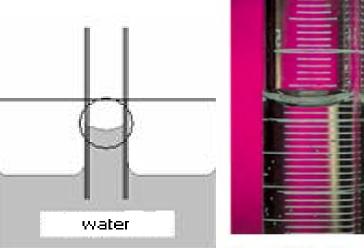


Figure 13-9 The meniscus, as observed in glass tubes with water and with mercury.

II. Low surface tension liquids

☑The attraction forces. Between the liquid molecules are greater than the attraction forces between the solid surface (capillary tube) and the liquid molecules. So, the Liquid will be goes down as in the figure.

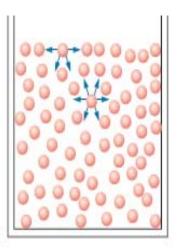
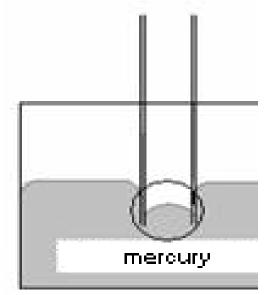
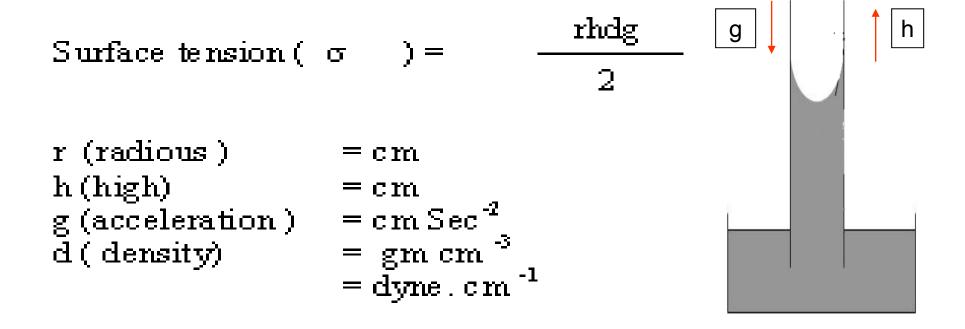


Figure 13-8 A molecular-level view of the attractive forces experienced by molecules at and below the surface of a liquid.





Method of measuring the surface tension (Capillary – rise method):





Ex. Acetone liquid goes up in capillary tube at 5.12 cm, the radius of the capillary tube is 0.0117cm and the density of acetoneis0.79gm.Cm-3.

Calculate the surface tension of acetone.

$$= \frac{\text{rhdg}}{2}$$
= \frac{1}{2} \times 0.0117 \times 5.12 \times 0.79 \times 981
= 23.2 \text{ dyne.cm}^{-1}.

the emulsifiers is materials using. for decrease.

The surface tension of the liquids.

It consists of two parts.

- 1-Hydrocaroon chain (non polar)
- 2- Function group (polar).

And it is using for:

- 1. Elimination the fats from the clothes by decreasing the surface tension between the water and the fats.
- 2. Decrease the surface tension between the plant surface and pesticides.
- 3. Control of mosquitoes by decreasing the surface tension of water surface using oils.
- 4. Decrease the surface tension of the sea waves using oils.
- Decrease the surface tension between the food and container surface using oils.



(7) Viscosity:

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"It can be defined as the resistance of liquid when its layers flowing through solid surface"

ex. "Water": Flow in fast through the solid surface comparing to "oils" flow in slowly this due to its viscosity.



- * The viscosity calculate by "Viscosity coefficient".
- •There is an irreversible relationship between the viscosity and the liquid velocity.

Ex. Oils and Glycerin has "High viscosity coefficient" while Benzene, Water and Alcohols has "low viscosity coefficient".

The symbol of the viscosity coefficient is "eta its unit is (Poise)

Of H_2O at 25 °C = 0.00895 poise.

The measurement of the liquids viscosity by "Viscometer" according to the equation:

$$= \frac{\Pi \operatorname{hdgr}^{t} t}{8 \operatorname{VL}}$$

 $\Pi = constant(3.14)$

L = Length of the capillary tube

T = time of flowing

d = liquid density

V = volume

r = radius

h = liquid high

g = acceleration

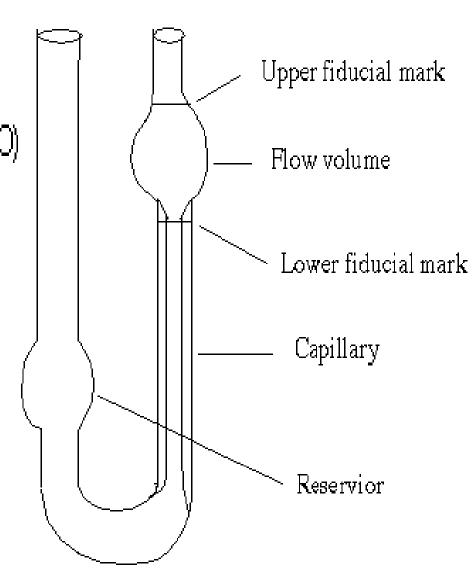
There is an easier way to measuring the liquids viscosity by " ostwald viscometer according to the equation:

$$\frac{\mathbf{\eta}_1}{\mathbf{\eta}_2} = \frac{\mathbf{d}_1 \mathbf{t}_1}{\mathbf{d}_2 \mathbf{t}_2}$$

 η_1 = viscosity coefficient of unknown liquid . η_2 = viscosity coefficient of standard liquid (H2O)

 d_1 = density of unknown liquid. d_1 = density of water.

t₁= Flow time of unknown liquid. t₂= Flow time of water.





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ex. The heptane's flowing in Ostwald viscometer at 64 sec while the water is flowing at 108 sec at the same conditions. Calculate the viscosity of Heptane

If : density of water = 1 (at $25 \, ^{\circ}$ C).

: density of Heptane = 0.689.

: Viscosity of water = 0.01 Poise.

$$\mathbf{m}_{1}$$
(Heptane)= 0.00412 Poise



