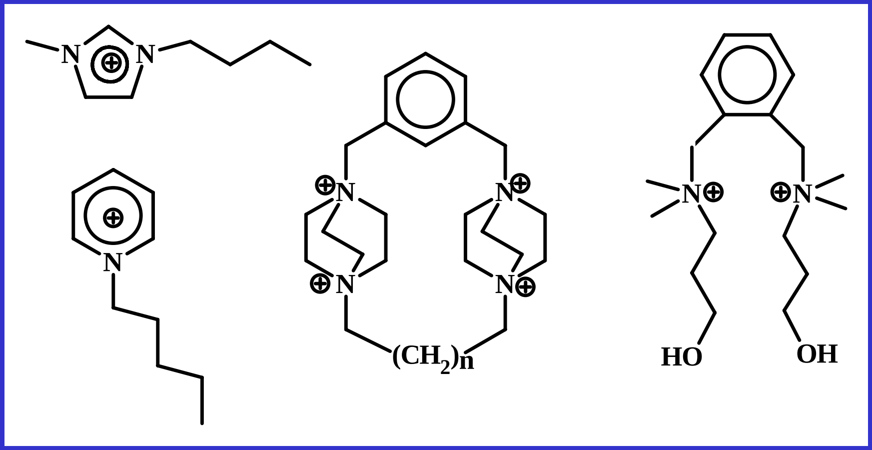
Liquids

Molecular – vdW forces, H-bonds

Metallic – melted metals, ions + electrons, electrostatic forces

Ionic – melted salts, FLINAK (LiF + NaF + KF), freely moving anions and cations, ion electric conductivity,
$EtNH_3^+ NO_3^-$ m.p. 12 °C



Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, PF_6^-, $SnCl_3^-$, BCl_3^-, BF_4^-, NO_3^-, $OSO_2CF_3^-$ (triflate), $CH_3C_6H_4SO_3^-$, $N(SO_2CF_3)_2^-$, PO_4^{3-}

Hole Theory of Liquids

Solids (molecular) – close packing in lattice, molecules touch, vdW radii

Liquids – same nearest-neighbor distances as in solids, lower density, coordination number decreases with increasing temperature
Ar (s) c.n. 12
Ar (l) c.n. 10 – 11 at melting, density lower by 12%
Ar (l) c.n. 4 at critical temperature

Liquids – free space (voids) in nearly close packed structure, molecules with a high E_{kin} move through the structure, molecules with a low E_{kin} engage in vdW interactions

Hole Theory of Liquids

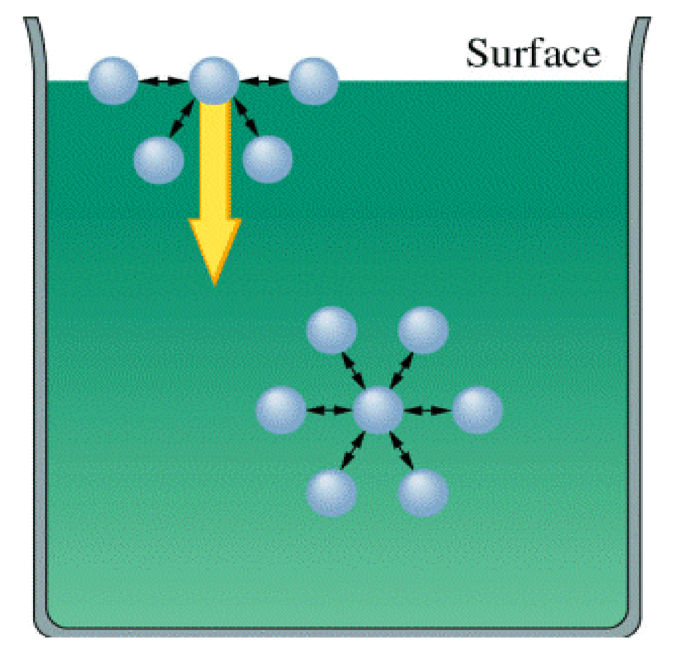
Two types of molecules in liquids:

1. molecules neighboring a vacation (hole) – similar to (g)
2. molecules surrounded by other molecules – similar to (s)

Structure of liquids is between regular structure of solids and random motion of gases.

E_{kin} of liquid molecules is too high to keep them in lattice positions, but too low to leave vdW interactions and escape from a container

Surface Tension



Molecules on a **surface** of a liquid interact with other molecules **inside** liquid – unequal forces

A force in a **surface** of a liquid, that keeps the surface area at minimum – spherical shape.

Surface Tension = Energy to form 1 m^2 of new surface
[$N\ m^{-1} = J\ m^{-2}$]

Surface Tension

Surface Tension = Energy to form new surface = to take molecules from inside a liquid (strongly held) and bring them to surface (weakly bound)

Free surface energy E

$E = \gamma S$
γ = surface tension [$\mathrm{N\ m^{-1} = J\ m^{-2}}$]
S = surface area

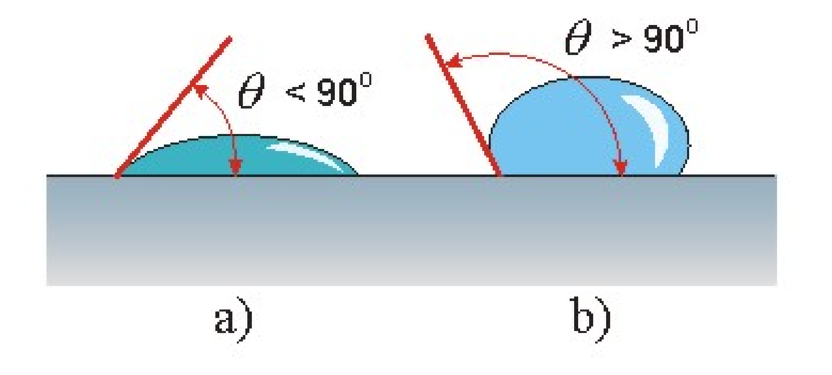
$F = \gamma l$ [$\mathrm{N\ m^{-1} = J\ m^{-2}}$]

$$\boxed{\gamma = \frac{dE}{dS}}$$

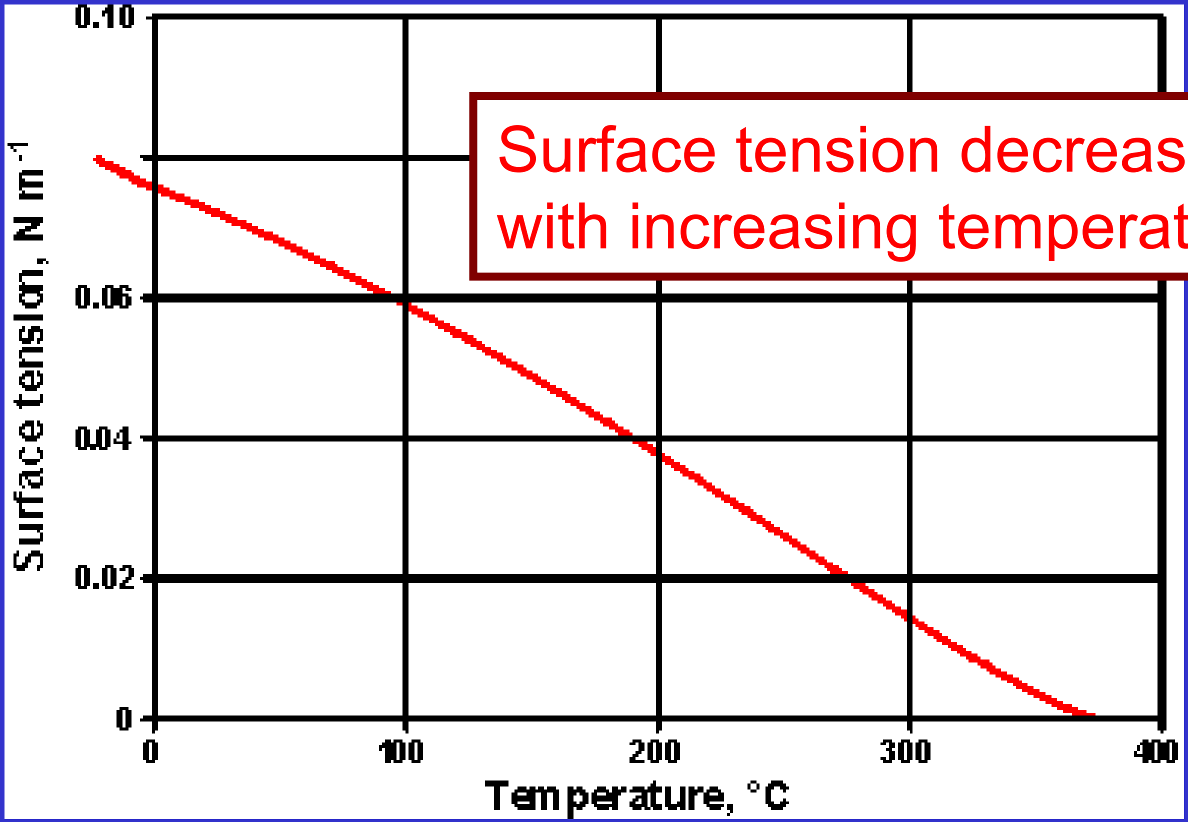
Surface Tension

Vodoměrka
Desinfection
Surfactants - soaps

Phase boundary (T = 20 °C)	γ, Surface tension [mJ m^{-2}]
Water / Air	72.75
Hg / Air	472
Benzene / Air	28.88
Water / Air (100 °C)	58.0

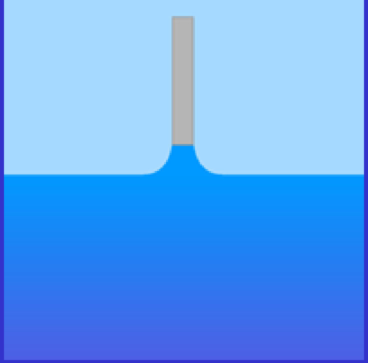


Surface Tension of Water



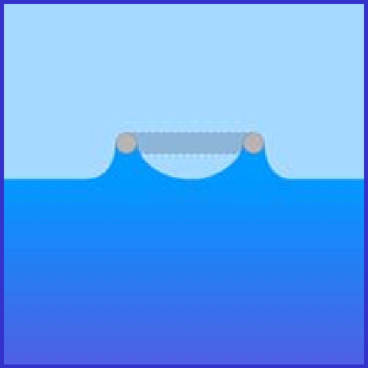
Surface tension decreases with increasing temperature.

Surface Tension Meaurements



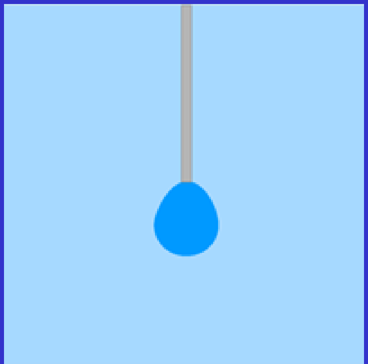
Tensiometer
Plate - Wilhelmy

$$\gamma = \frac{dE}{dS}$$



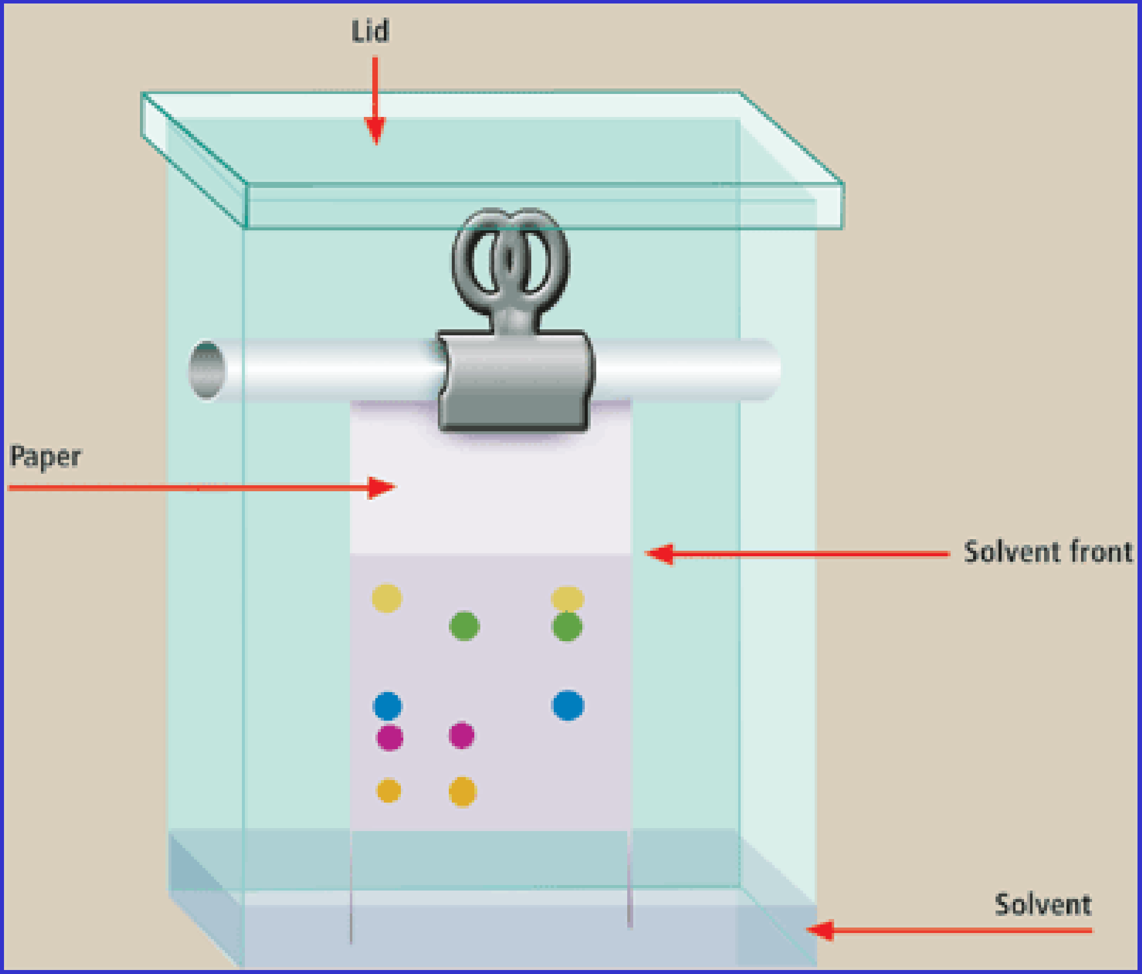
Tensiometer
Ring – DeNouy

$2 \pi D \gamma = F$



Hanging droplet

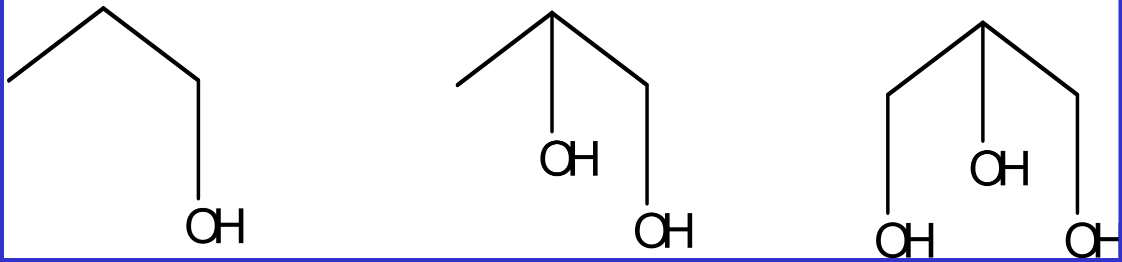
Paper Chromatography



Viscosity

Internal friction, resistance to flow

Increases with intermolecular forces:



Increases with chain length, entanglement

Decreases with increasing temp $\eta = A \exp(E / RT)$

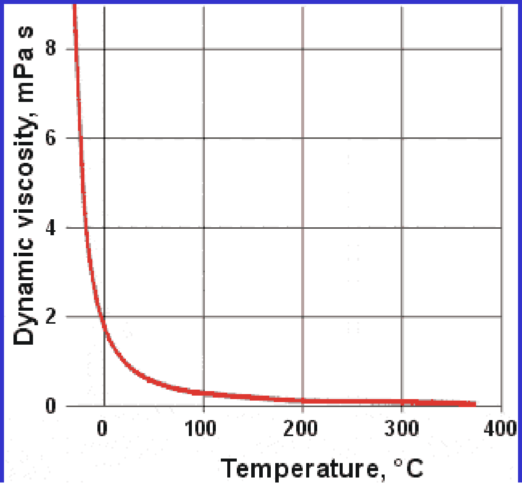
Stokes equation

$F = 6 \pi \eta r v$

η = viscosity [kg m^{-1} s^{-1}]

r = ball radius

v = speed



Evaporation and Condensation

Molecules at surface with sufficient E_{kin} and correct movement direction can overcome vdW forces and surface tension and leave liquid to gas phase even below boiling point

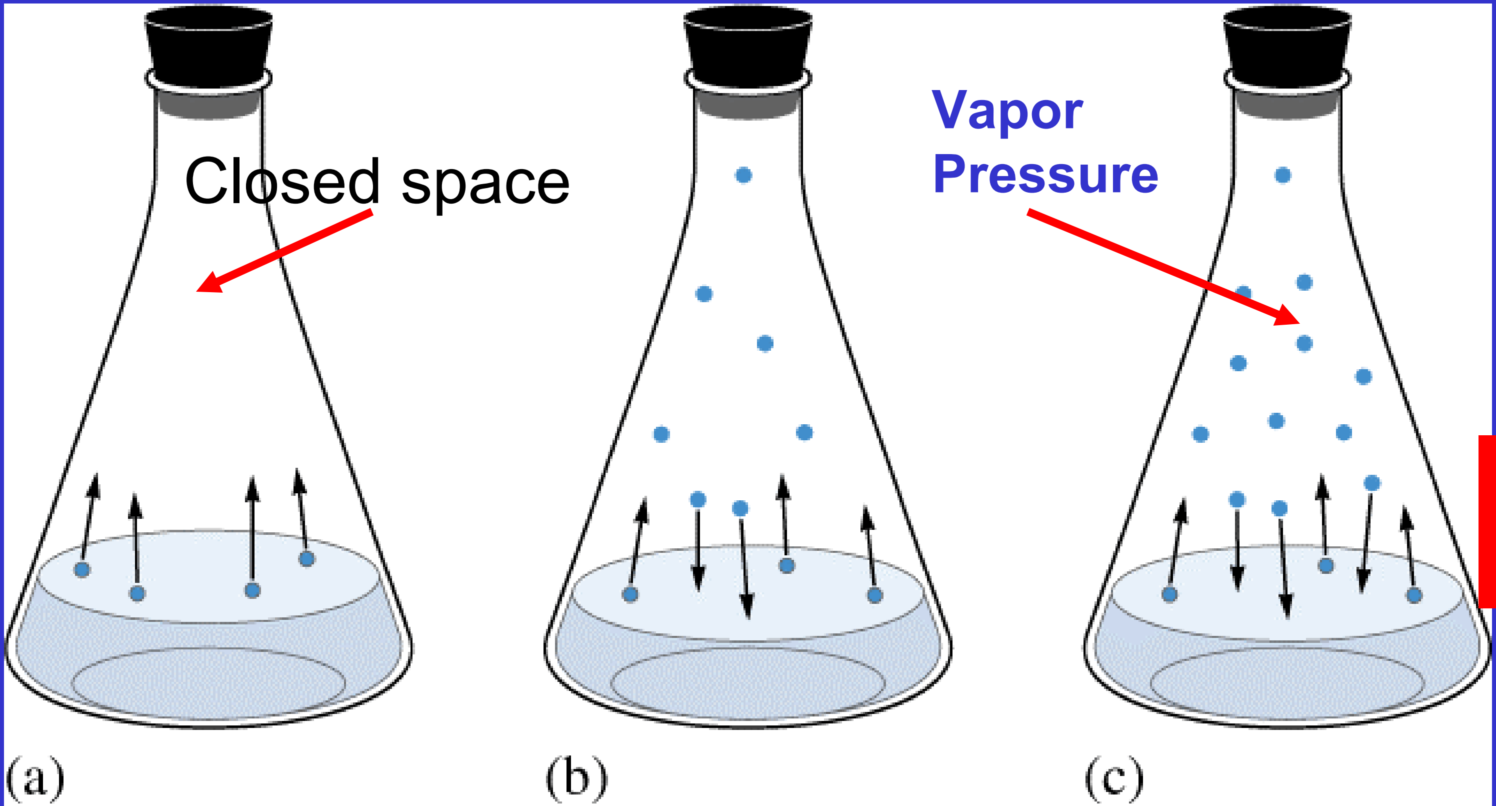
Evaporation of liquid = **Energetically rich molecules** leave – liquid cools

Condensation = collisions of vapor molecules (g) with surface (l), loss of E_{kin}, molecules trapped by vdW forces into (l)

vaporization and condensation enthalpy

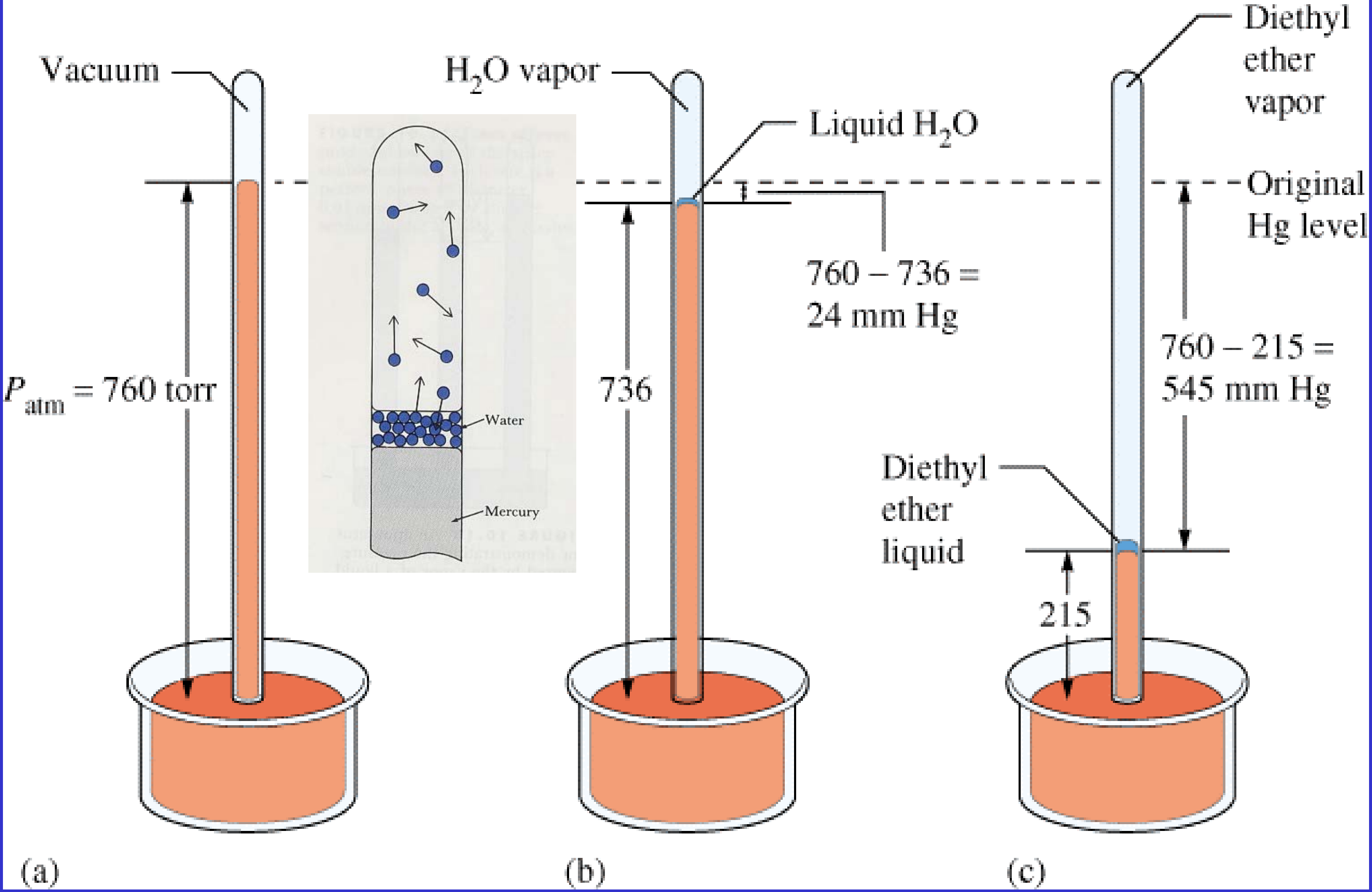
$\Delta H_{vap} > 0$ endo $\Delta H_{\text{condí}} < 0$ exo

Vapor Pressure



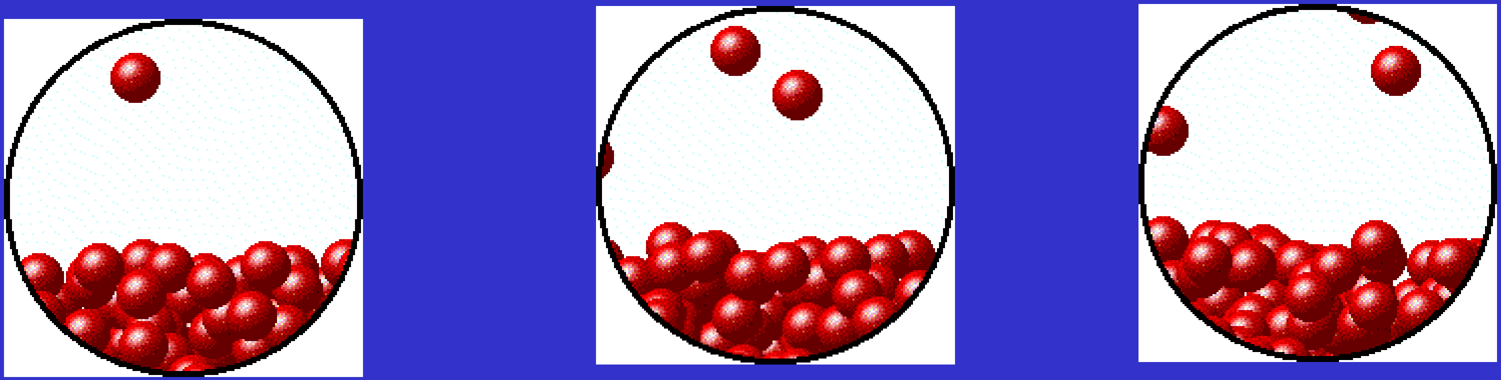
Dynamic equilibrium

Vapor Pressure



Vapor Pressure

Vapor pressure increases with temp (760 torr = 101.325 kPa)

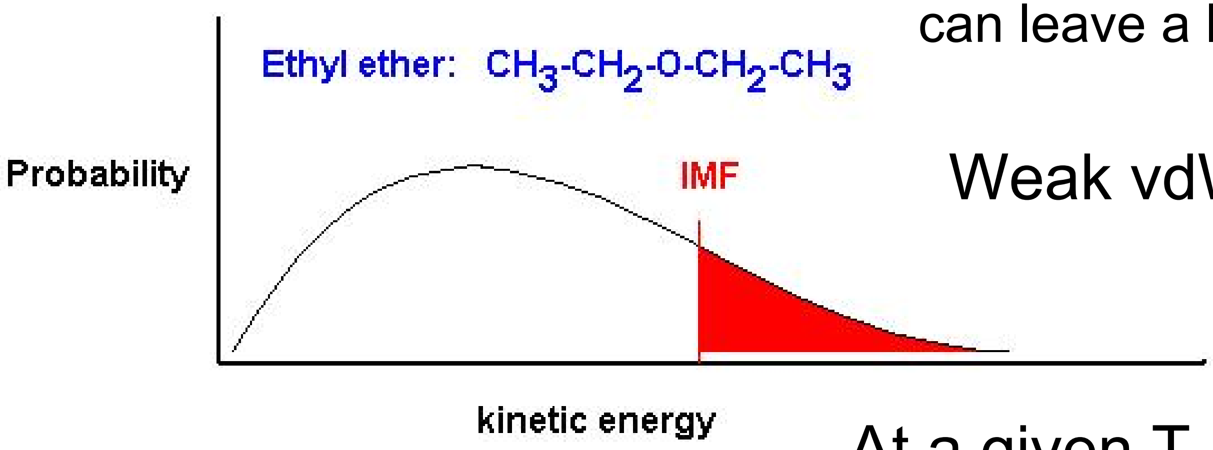


Temp. Compound	20 ºC	25 ºC	50 ºC
Water	17.5	23.8	92.5
Diethylether	377	470	1325

[torr]

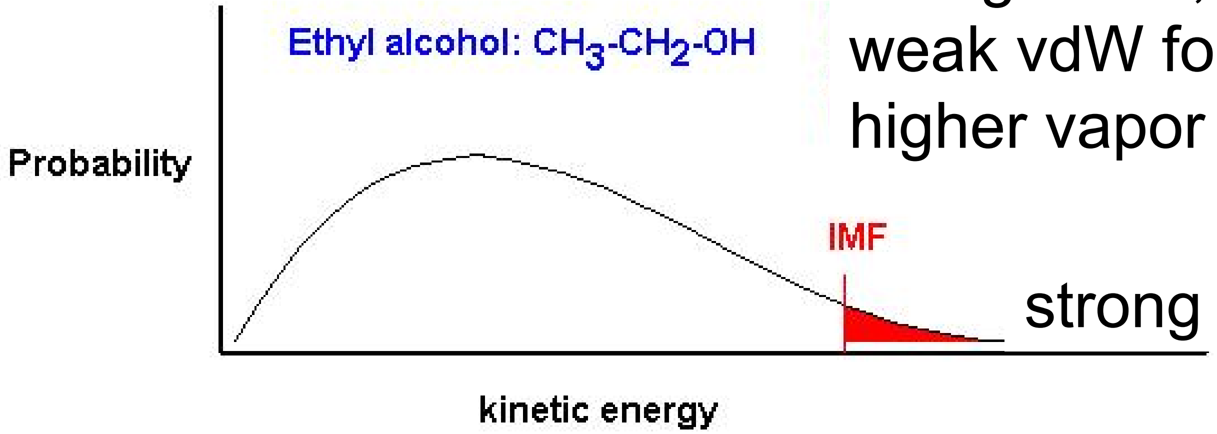
Vapor Pressure and Kinetic Theory

Only molecules with $E_{kin} > E_{imf}$ can leave a liquid



Weak vdW forces

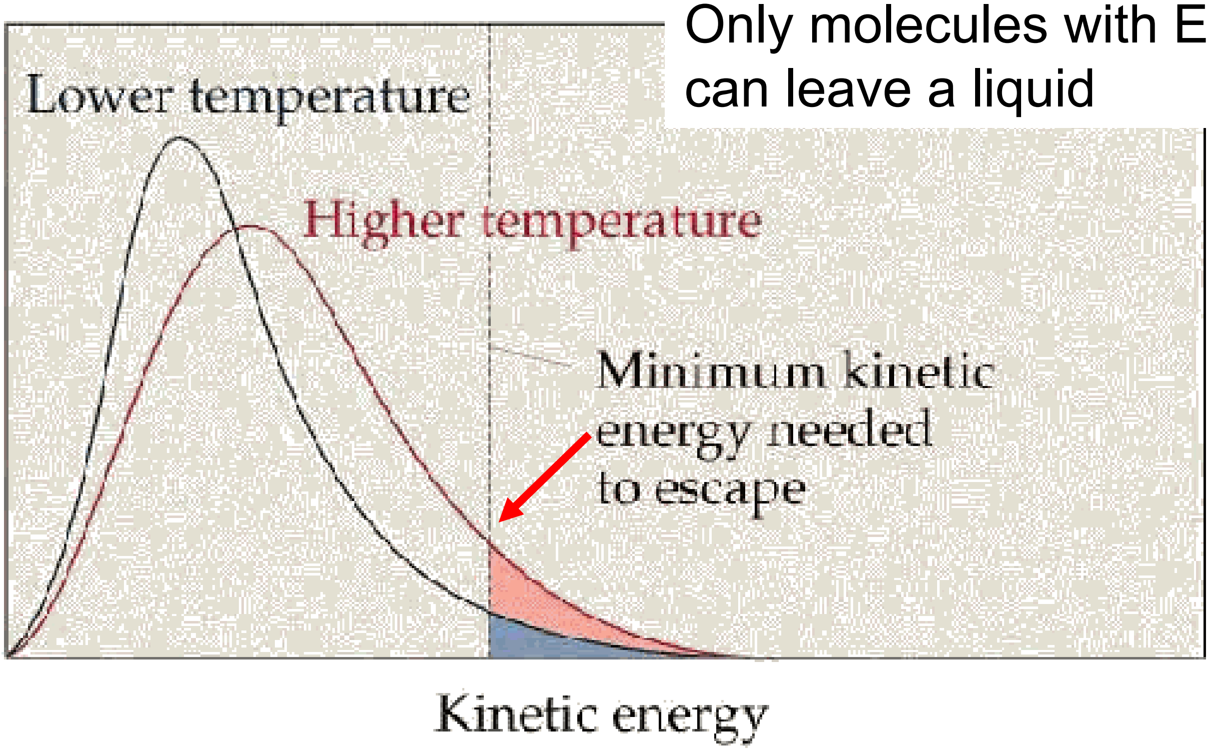
At a given T, liquids with weak vdW forces have higher vapor pressure



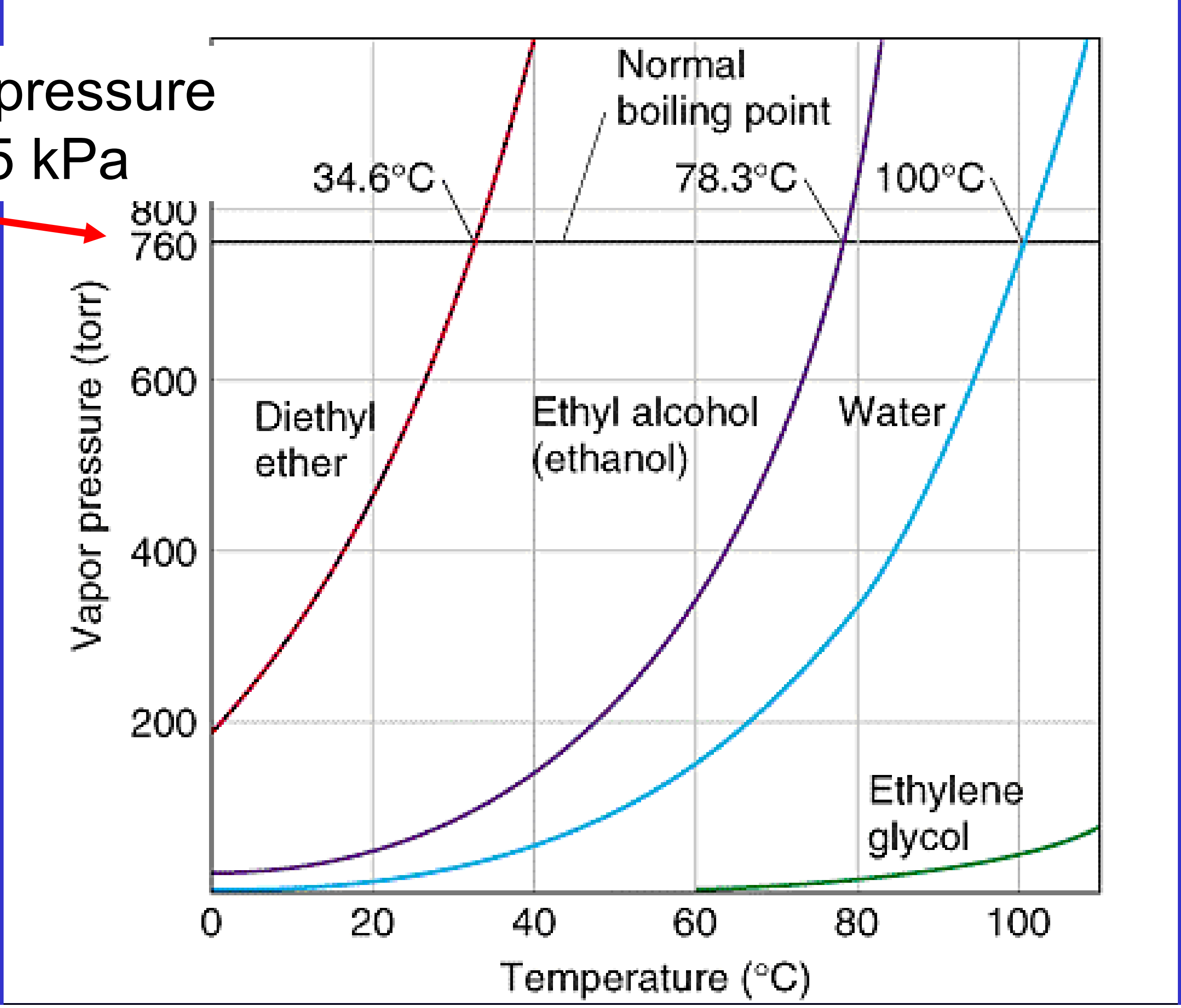
strong vdW forces

Vapor Pressure and Temperature

Only molecules with $E_{kin} > E_{imf}$ can leave a liquid



Vapor Pressure



Normal pressure
101.325 kPa

Boiling point = temp, at which vapor pressure equals ambient pressure

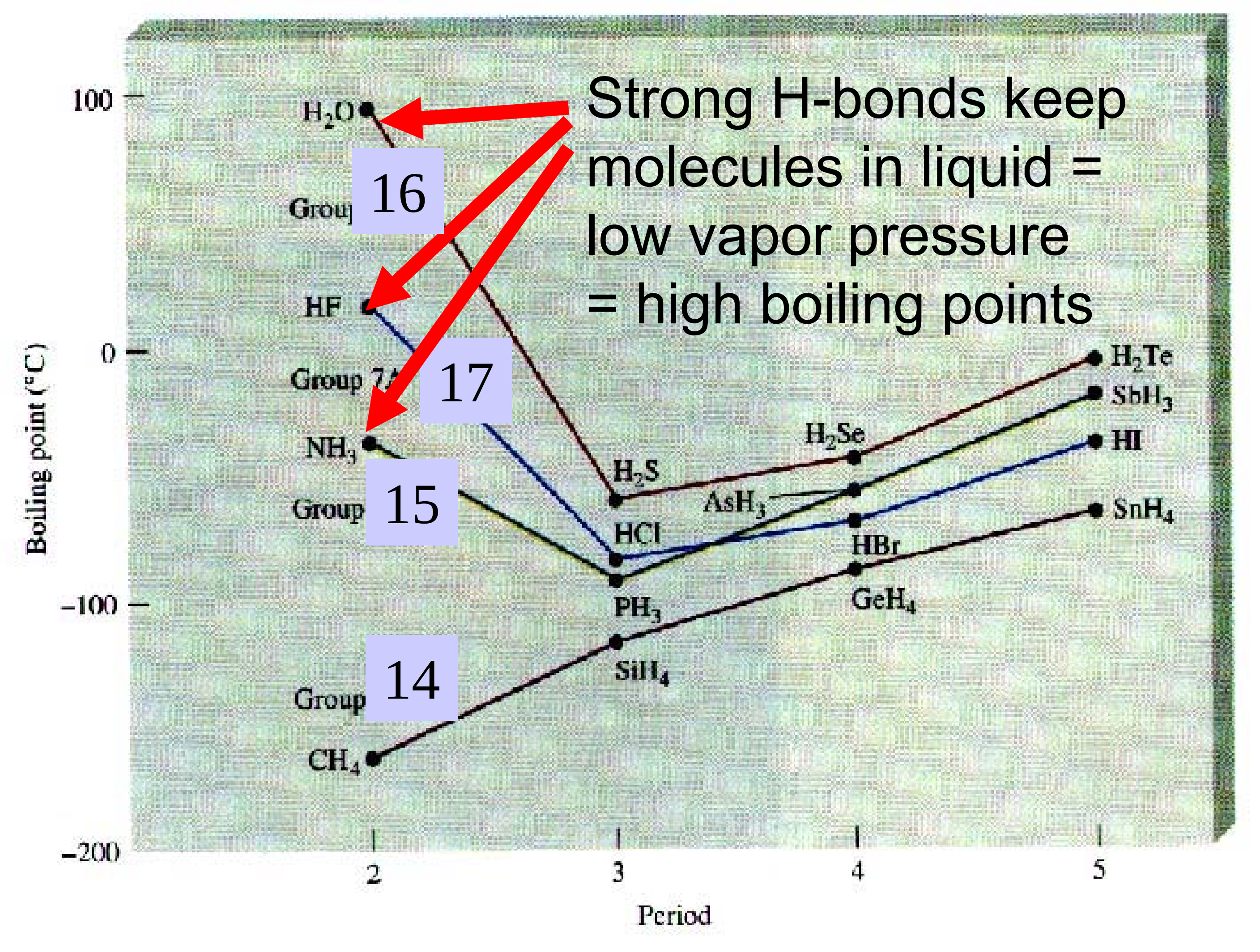
Normal boiling point = temp, at which vapor pressure equals ambient pressure of 101.325 kPa

Sublimation point = temp, at which vapor pressure of a solid equals ambient pressure

Normal sublimation point = temp, at which vapor pressure of a solid equals ambient pressure of 101.325 kPa

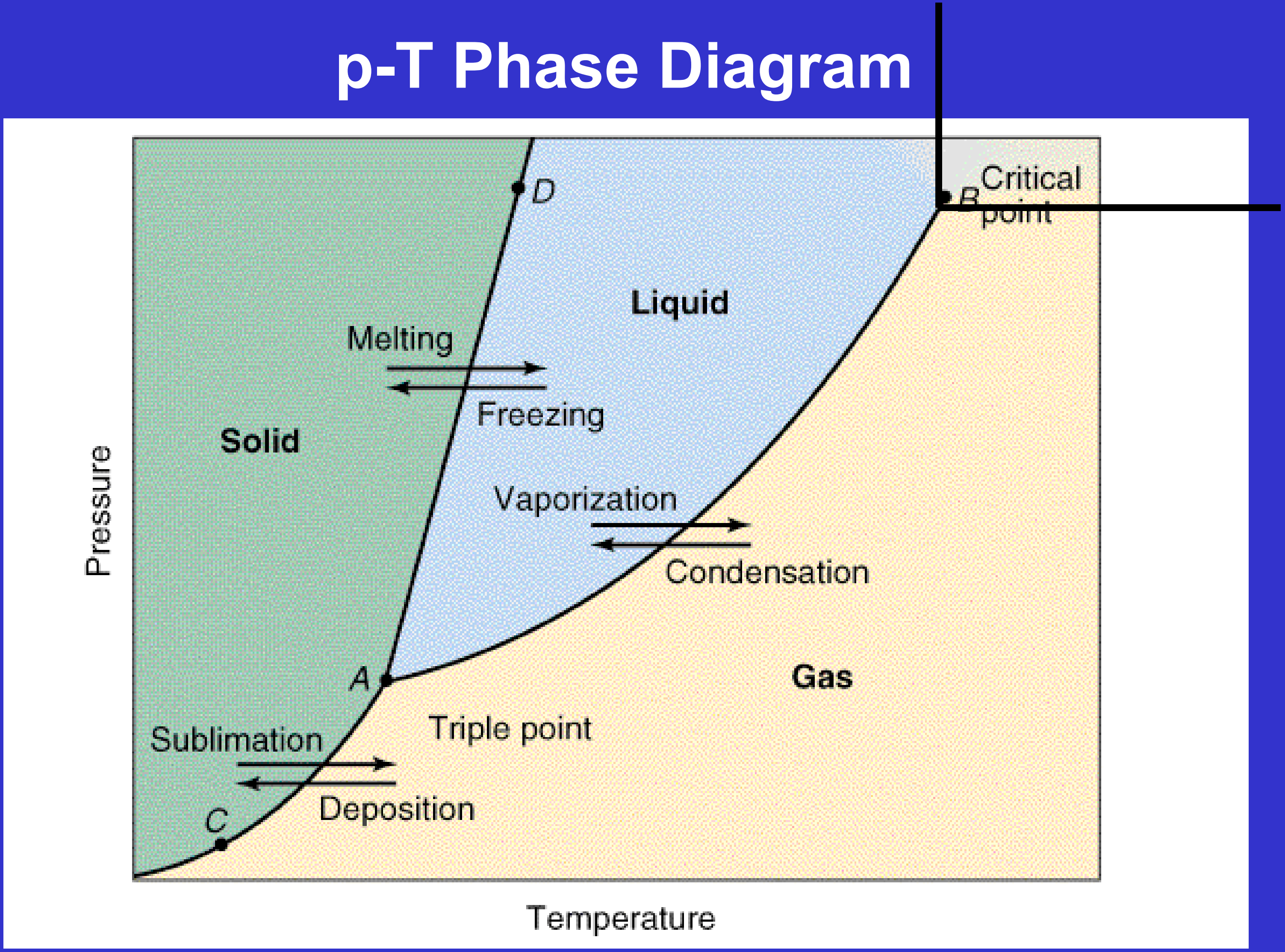
Boiling and sublimation can be induced by heating or lowering ambient pressure

Normal Boiling Points of Group 14– 17 Hydrides



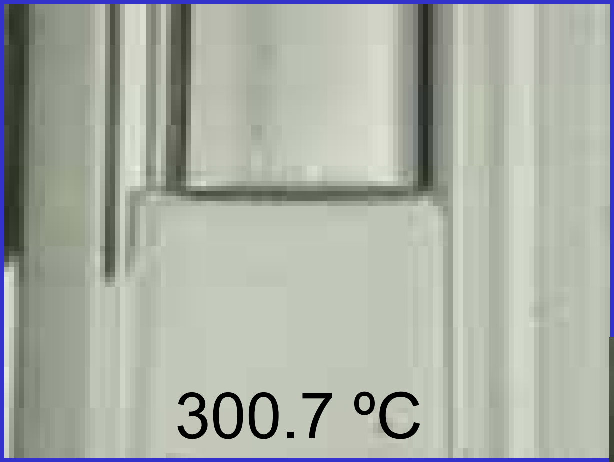
Strong H-bonds keep molecules in liquid = low vapor pressure = high boiling points

p-T Phase Diagram

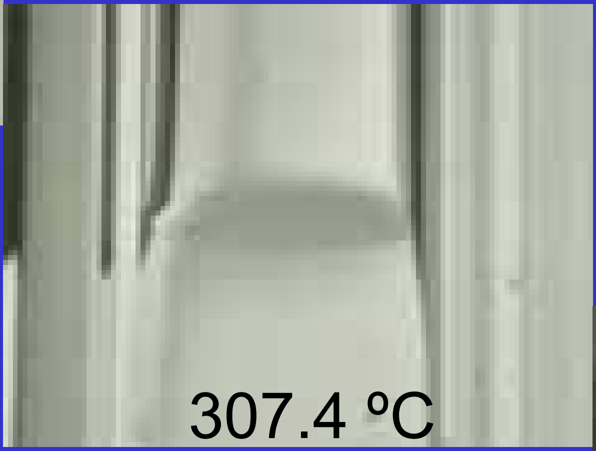


Critical Point of Benzene

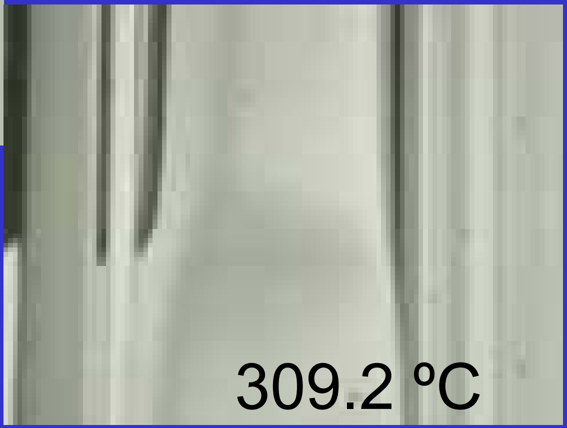
Phase boundary (meniscus)
between l and g disappears



300.7 ºC

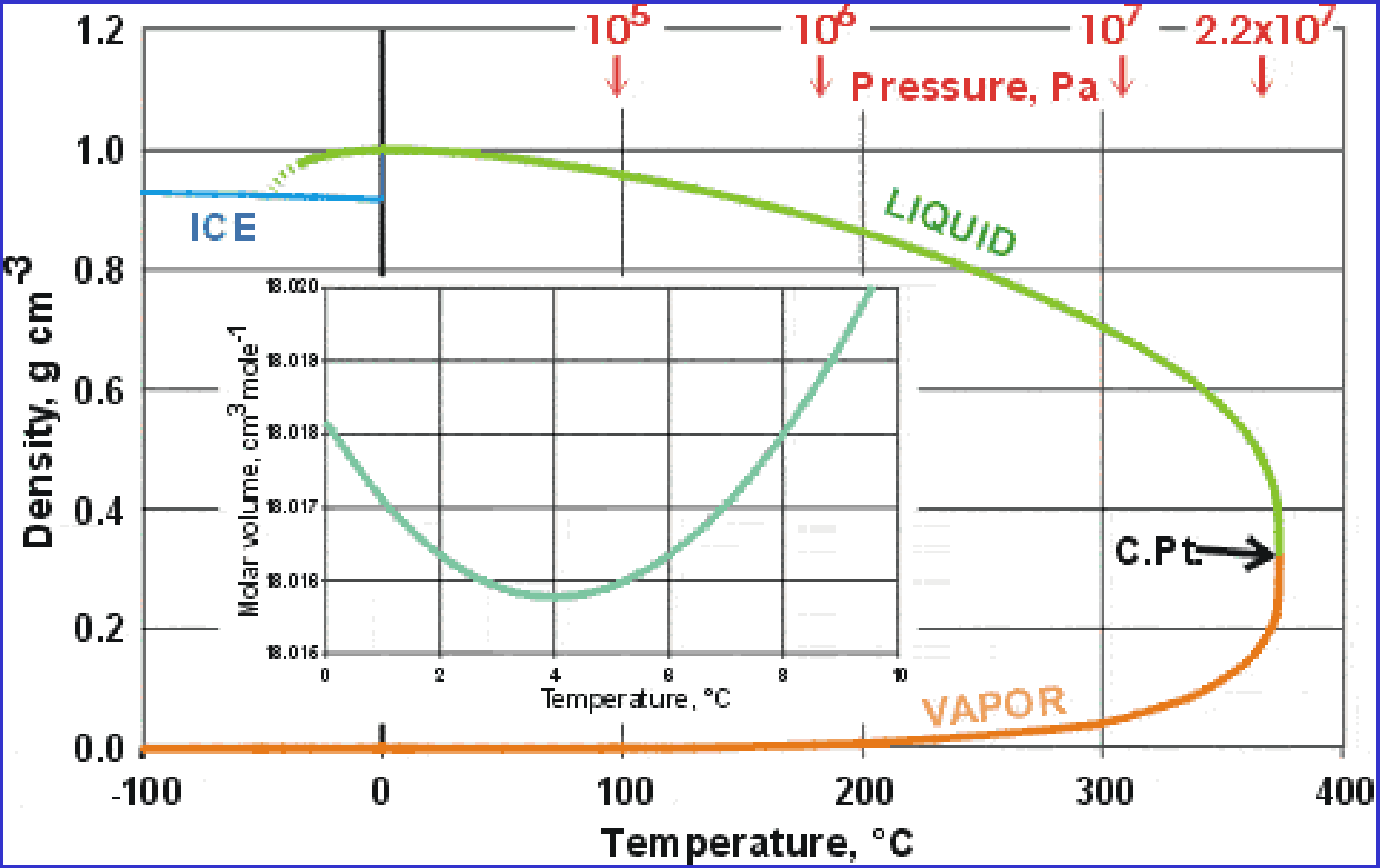


307.4 ºC

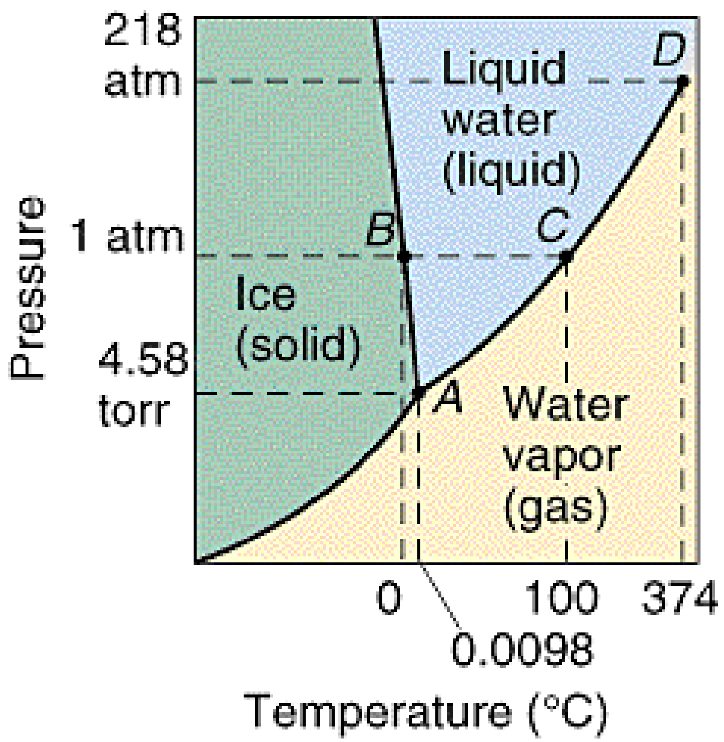


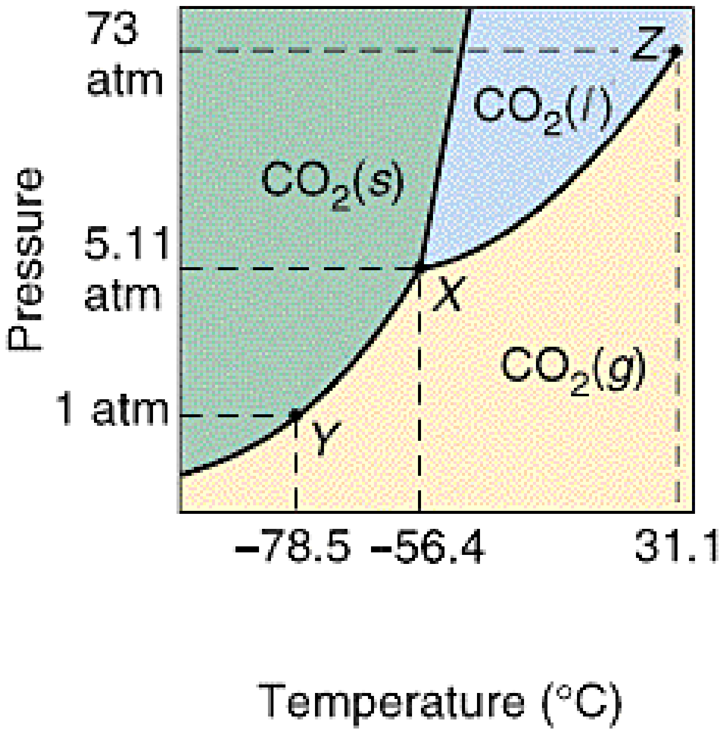
309.2 ºC

Water Density (g, l, s)



p-T Phase Diagram





Increasing pressure decreases melting point of water = anomaly

Increasing pressure causes solidification of liquid

Clausius-Clapeyron Equation

Clapeyron eq. of phase transition

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

For l-g equil:

1) $V_m(g) \gg V_m(l)$, then $\Delta V_m = V_m(g)$

2) $V_m(g)$ from id. gas eq.

$$V_m(g) = \frac{RT}{p}$$

Differential Clausius-Clapeyron eq.

$$\frac{d \ln p}{dT} = \frac{\Delta H_m}{RT^2}$$

Integrated Clausius-Clapeyron eq.

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Antoine Equation

$$\log_{10} p = A - \frac{B}{C + T}.$$

p = vapor pressure (bar)
T = temp (K)

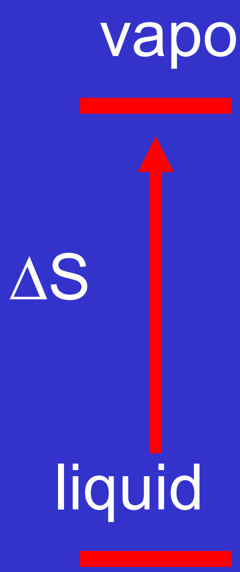
Water

Temp. interval (K)	A	B	C
379. - 573.	3.55959	643.748	-198.043
273. - 303.	5.40221	1838.675	-31.737
304. - 333.	5.20389	1733.926	-39.485
334. - 363.	5.07680	1659.793	-45.854
344. - 373.	5.08354	1663.125	-45.622

Trouton Rule

$\Delta G = 0$ in equlibrium, at phase transitions

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



vapor

ΔS

liquid

For different liquids (nonpolar) at normal boiling point, **vaporization** molar entropy is roughly the same:

$$\Delta S^{0}_{m,vap} = \frac{\Delta H^{0}_{m,vap}}{T_b} = 90\,JK^{-1}mol^{-1}$$

Not true for water at 100 ºC – very strong H bonds = ordered structure = small entropy of liquid water

$\Delta S^{0}_{vap} = 109\ J\ K^{-1}\ mol^{-1}$

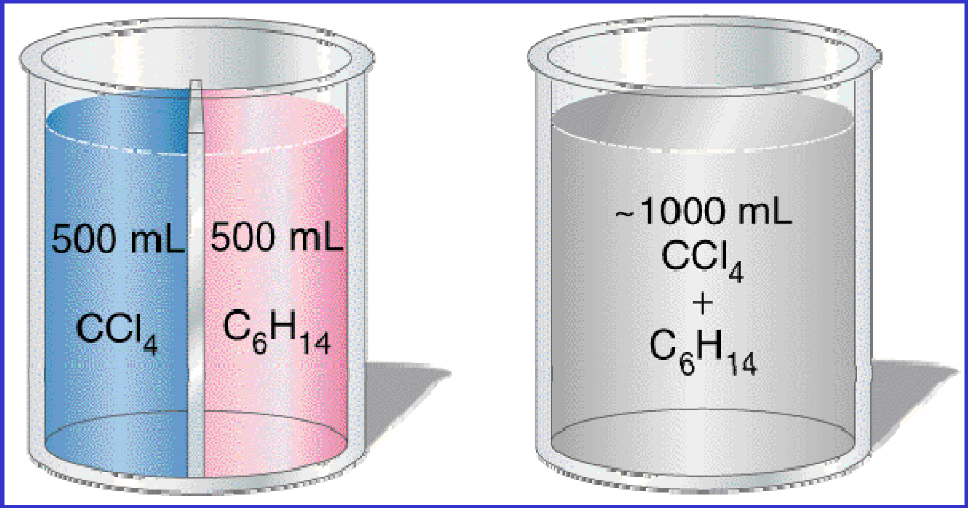
Diffusion

In liquids and gases, in solids at increased temperature

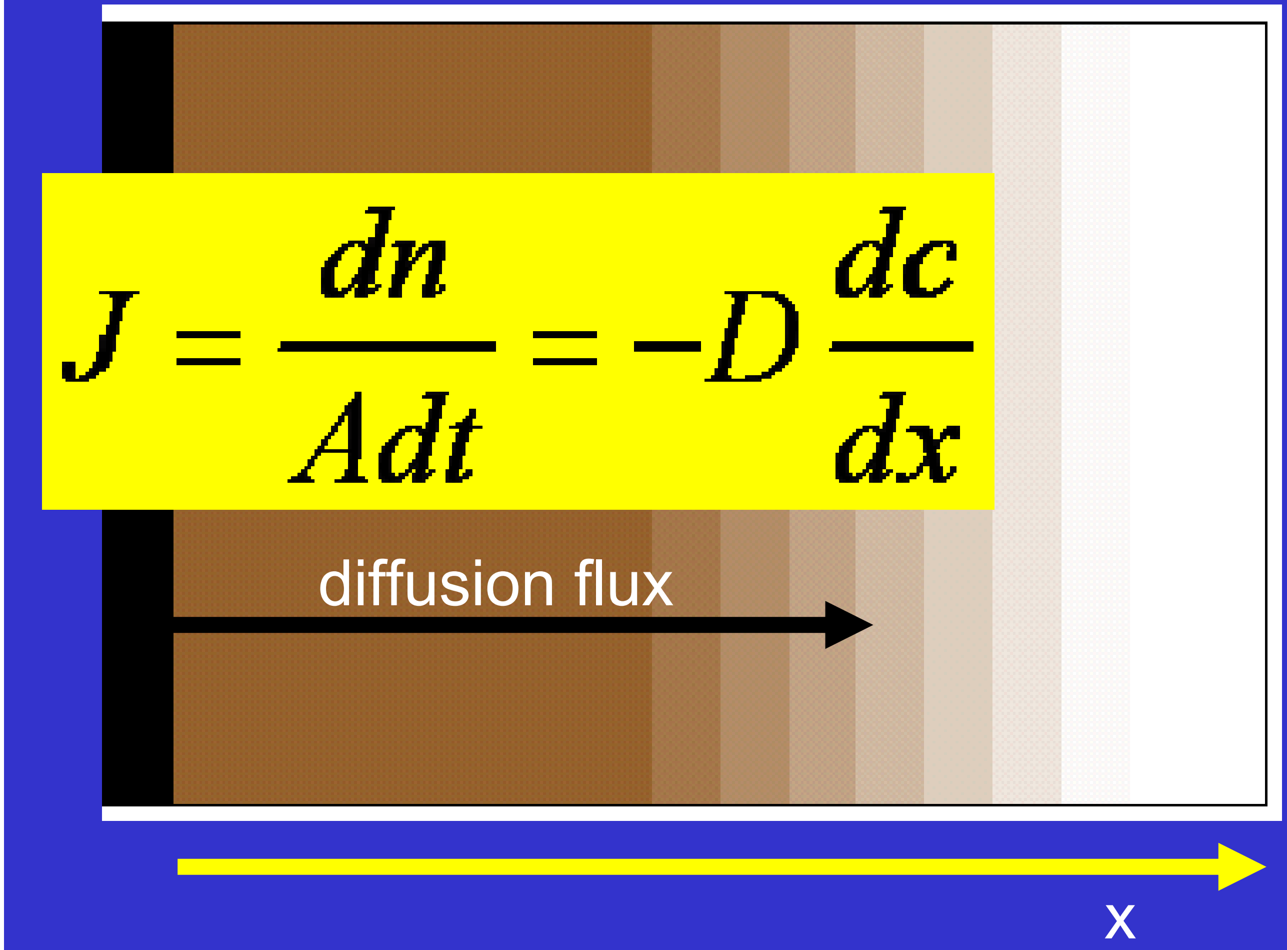
Spontaneous mixing of compounds
Mass transfer
Equalization of concentrations
Result of random movements of molecules

First Fick's law for diffusion flux J

$$J = \frac{dn}{Adt} = -D\frac{dc}{dx}$$



First Fick's Law



$$J = \frac{dn}{A\,dt} = -D\,\frac{dc}{dx}$$

J = diffusion flux
[mol s^{-1} m^{-2}]

n = molar amount [mol]

D = diffusion coeficient
[m^2 s^{-1}]

dc/dx = gradient of concentration

A = area [m^2]