

CHEMICAL POTENTIAL

The concept of calculation of the chemical potential in one- and multi-component systems

- I. Chemical potential of an ideal gas
- II. Chemical potential of real gases. Fugacity
- III. Chemical potential of liquids
- IV. Chemical potential in multicomponent systems.
The Gibbs–Duhem equation
- V. Ideal mixtures. The Raoult and Henry laws
- VI. Real mixtures and solutions

CHEMICAL POTENTIAL

- **G Gibbs free energy** has been introduced to characterize the equilibrium state of spontaneous processes.
- The calculations are more straightforward if the partial derivative of G with respect to the composition of the system is used: this will be called **chemical potential**.
- The condition of equilibrium in all systems: the chemical potentials of a component in each phase must be the same.

CHEMICAL POTENTIAL

- The chemical potential of a pure substance is the same as the molar Gibbs free energy:

$$\mu = \left(\frac{\partial nG_m}{\partial n} \right)_{T,p} = G_m$$

- The chemical potential μ_i of component i in a mixture is the partial molar Gibbs free energy:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$

CHEMICAL POTENTIAL

Chemical potential under different conditions:

definition of μ_j with G :
(isothermal, isobaric)

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{T,p,n'}$$

definition of μ_j with U :
(isochoric, isentropic)

$$\mu_j = \left(\frac{\partial U}{\partial n_j} \right)_{V,S,n'}$$

definition of μ_j with H :
(isobaric, isentropic)

$$\mu_j = \left(\frac{\partial H}{\partial n_j} \right)_{p,S,n'}$$

definition of μ_j with A :
(isochoric, isothermal)

$$\mu_j = \left(\frac{\partial A}{\partial n_j} \right)_{V,T,n'}$$

U , H , A and G are not only state functions but also thermodynamic potential functions.

I. CHEMICAL POTENTIAL OF AN IDEAL GAS

- The simplest system: the **ideal gas**.
- Its Gibbs free energy at pressure p and temperature T :

$$G = G^\theta + nRT \ln \left(\frac{p}{p^\theta} \right)$$

G^θ is the standard molar free energy of the gas (at $p^\theta = 1$ bar and given T).

- The chemical potential at pressure p is obtained by derivation with respect to n :

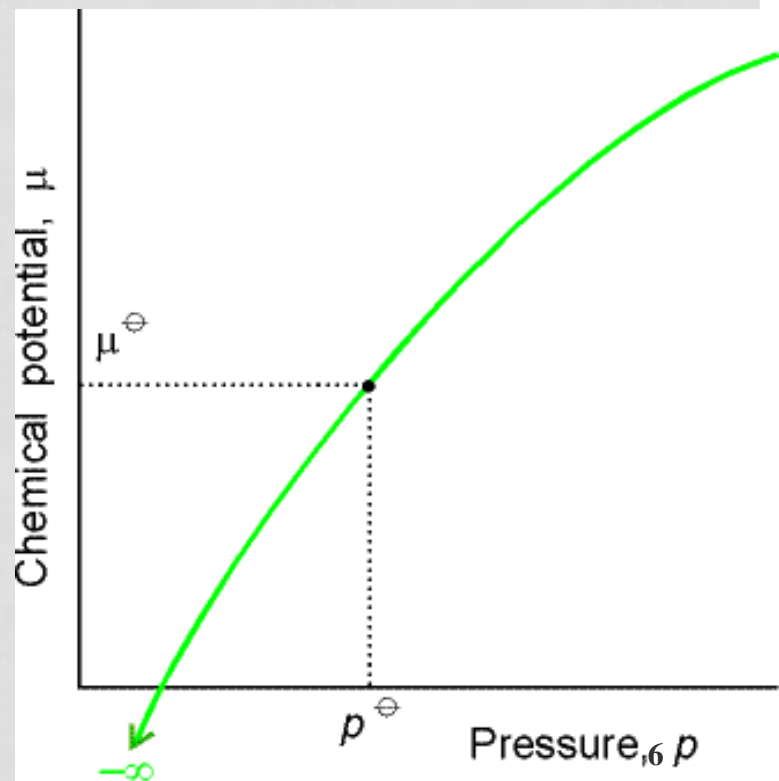
$$\mu = \mu^\theta + RT \ln \left(\frac{p}{p^\theta} \right)$$

μ^θ is the standard chemical potential: the standard molar free energy of the pure gas (at $p^\theta = 1$ bar and a given T).

I. CHEMICAL POTENTIAL OF AN IDEAL GAS

- The standard state is reached at p^\ominus .
- If $p \rightarrow 0$, then $\mu \rightarrow -\infty$.
- On a graph:

$$\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right)$$



II. CHEMICAL POTENTIAL OF A REAL GAS

- The **definition of fugacity**: for **real gases**, the measured pressure p in the formula giving the pressure dependence of the chemical potential is replaced by **effective pressure**, which is called **fugacity (f)**:

$$\mu = \mu^\theta + RT \ln \left(\frac{f}{p^\theta} \right)$$

$$\mu = \mu^\theta + RT \ln \left(\frac{p}{p^\theta} \right)$$

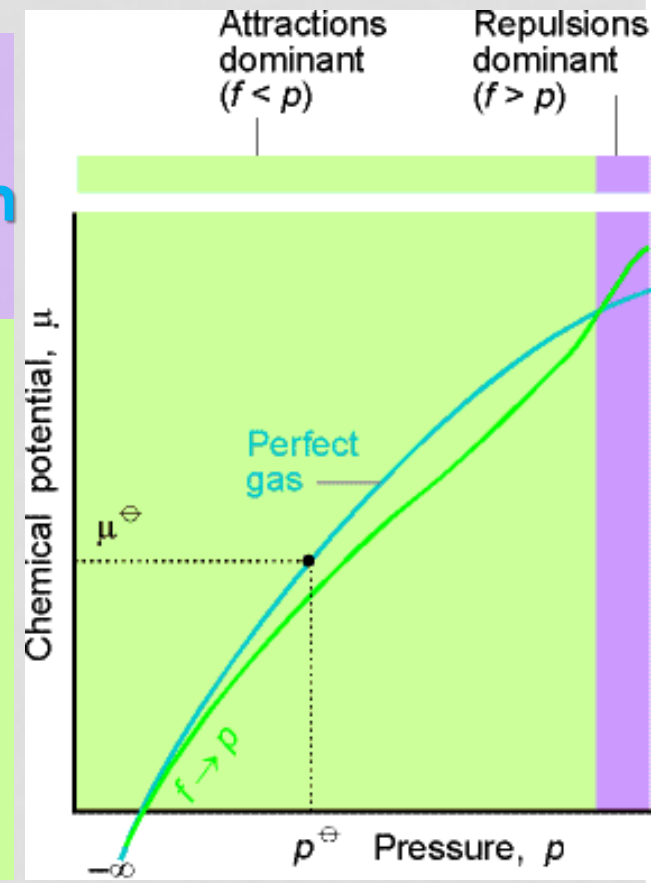
II. CHEMICAL POTENTIAL OF A REAL GAS

- Two issues should be settled.
 - **the relationship between fugacity and pressure:**
 $f = \gamma p$ γ is the dimensionless fugacity coefficient
 - the **standard state p^θ of a real gas**: a hypothetical state in which the pressure p^θ and it behaves like an ideal gas (no interactions).
- $RT \ln \gamma$ is a measure of the intermolecular forces.

$$\mu = \mu^\theta + RT \ln \left(\frac{p}{p^\theta} \right) + RT \ln \gamma$$

I. CHEMICAL POTENTIAL OF A REAL GAS

- At high pressure, repulsion forces are dominant, so **the chemical potential of real gases is higher than for an ideal gas.**
- At intermediate pressure, attraction is dominant, so **the chemical potential is lower than for an ideal gas.**
- As $p \rightarrow 0$, μ will be the same as for an ideal gas, as no significant intermolecular interaction is possible.

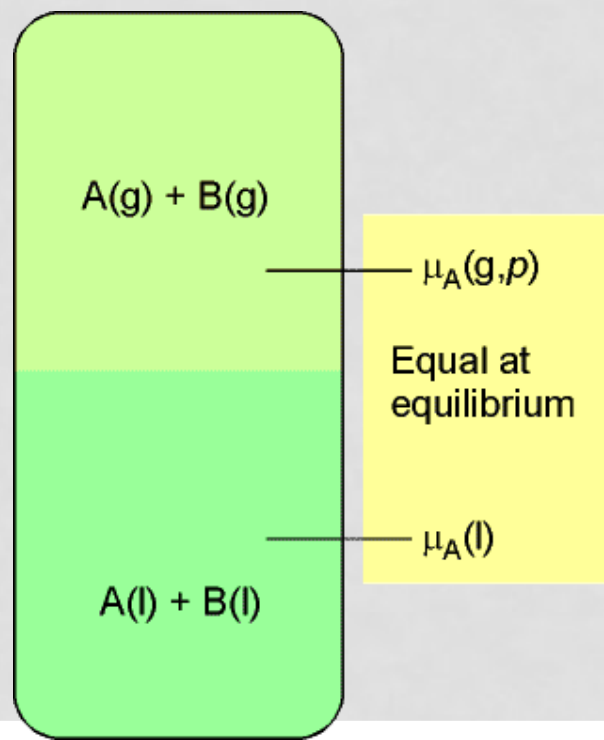


III. CHEMICAL POTENTIAL OF LIQUIDS

- How does μ depend on the composition?
 - Starting point: in equilibrium, μ is equal in the liquid and gas phases:

$$\mu(l) = \mu(g) = \mu^\theta(g) + RT \ln \left(\frac{p}{p^\theta} \right)$$

- The equality of μ values is true both for the solute (B) and the solvent (A).



IV. MULTICOMPONENT SYSTEMS.

THE GIBBS-DUHEM EQUATION

- In a multicomponent system (e.g. mixture), the **Gibbs free energy is additive**, it can be obtained as the sum of the partial molar Gibb free energies (chemical potentials) of the individual components:

$$G = n_A \mu_A + n_B \mu_B$$

- If only the compositions changes (at constant T and p):

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

- But from the definition: $dG = \mu_A dn_A + \mu_B dn_B$
- Combining the two gives:

$$0 = n_A d\mu_A + n_B d\mu_B$$

V. IDEAL MIXTURES. RAOULT'S AND HENRY'S LAW

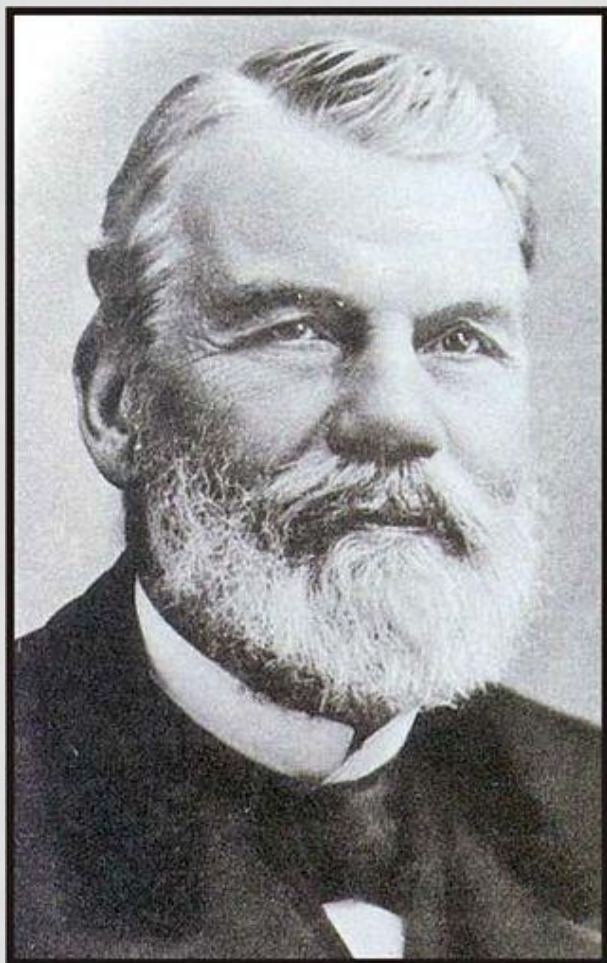
- For pure A (*):
$$\mu_A^*(l) = \mu_A^*(g) = \mu_A^\theta + RT \ln \left(\frac{p_A^*}{p^\theta} \right)$$
- A in solution:
$$\mu_A(l) = \mu_A(g) = \mu_A^\theta + RT \ln \left(\frac{p_A}{p^\theta} \right)$$
- By subtracting the two equations:
$$\mu_A(l) = \mu_A^*(l) + RT \ln \left(\frac{p_A}{p_A^*} \right)$$
- Based on experimental results, **Raoult** formulated a law (for „the mixtures of related substances“): $p_A = x_A p_A^*$
- For **ideal mixtures**, the following can be written (this is also a definition):
$$\mu_A(l) = \mu_A^*(l) + RT \ln(x_A)$$

V. IDEAL MIXTURES. RAOULT'S AND HENRY'S LAW

- **For an ideal mixture**, both components (A and B) follow **Raoult's law**:

$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^*$$

-
- There are so-called **ideal dilute solutions** where the partial pressure of the solute is directly proportional to its molar fraction and the proportion constant – instead of the pressure of the solute – is another pressure-like constant (K_B): $p_B = x_B K_B$
 - This is **Henry's law** (valid mainly for dissolved gases). K_B is called Henry's constant (and is different from the vapor pressure of the pure solute).



François-Marie Raoult

1830 – 1901

French chemist



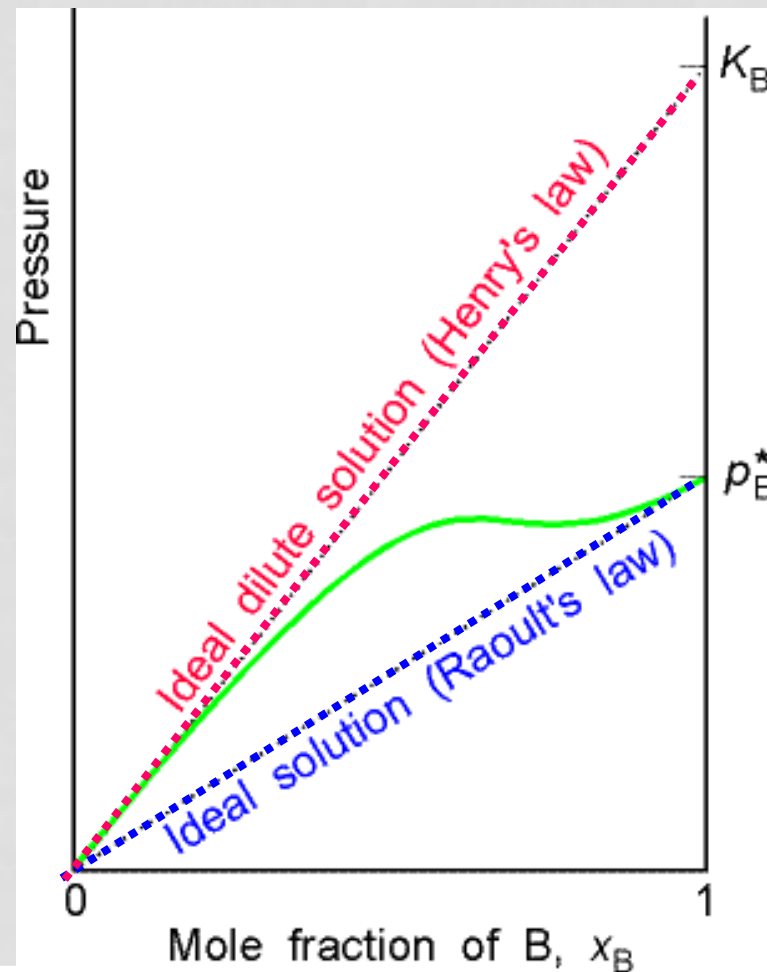
William Henry

1774 – 1836

English chemist

V. IDEAL MIXTURES. RAOULT'S AND HENRY'S LAW

- Validities of **Raoult's law** and **Henry's law**:



VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

- For real gases, fugacity (effective pressure, $f = \gamma p$) was used instead of pressure.
- For real mixtures and solutions – in order to keep the simple formalism of thermodynamics – activity (a) and activity coefficient (γ) are used instead of concentration (x_A).
 - $a_A = \gamma_A x_A$
 - $\mu_A(l) = \mu_A^*(l) + RT \ln a_A$
 - $\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$

VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

- Standard states (summary):

Component	Standard state	Chemical potential	kLimits
solvent A (Raoult's law)	pure solvent	$\mu_A = \mu_A^* + RT \ln a_A$ $a_A = p_A / p_A^* \text{ and}$ $a_A = \gamma_A x_A$	$\gamma_A \rightarrow 1$ when $x_A \rightarrow 1$ (pure solvent)
solute B (Henry's law)	pure solute (hypothetic state)	$\mu_B = \mu_B^\dagger + RT \ln a_B$ $a_B = p_B / K_B \text{ and}$ $a_B = \gamma_B x_B$	$\gamma_B \rightarrow 1$ when $x_B \rightarrow 0$

THERMODYNAMICS OF ONE-COMPONENT SYSTEMS

- I. Phase diagrams
- II. Phase stability and phase transitions
- III. The use of chemical potential to describe the equilibria in one-component multiphase systems
- IV. The effect of pressure on phase equilibria
- V. The effect of temperature on phase equilibria. The Clapeyron equation
- VI. Liquid-vapor systems: Clausius–Clapeyron equation.
- VII. Ehrenfest classification of phase transitions
- VIII. Surface tension. Curved surface. Capillary action

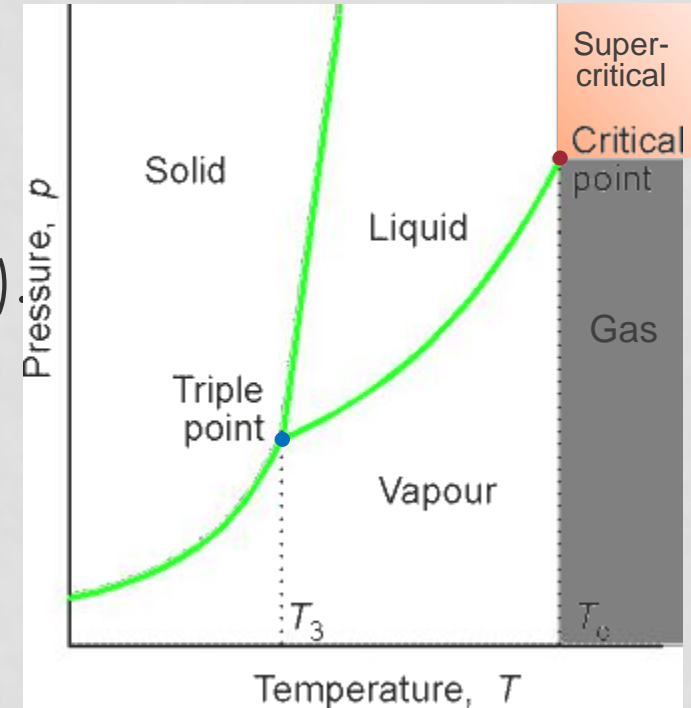
THERMODYNAMICS OF ONE-COMPONENT SYSTEMS

Principles of discussion:

- **Equilibrium systems (states) are described and studied.** (*Phases are stable or phase transitions happen depending on T , p , V and x_i .*)
 - In equilibrium, chemical potentials (μ) for all components in all phases are the same.
 - Equilibrium exists only in a **closed system**.
- **The changes (phase transitions) are reversible.** (*Phase transitions between solid phases are often irreversible.*)
 - The time needed for a phase transition is not discussed.

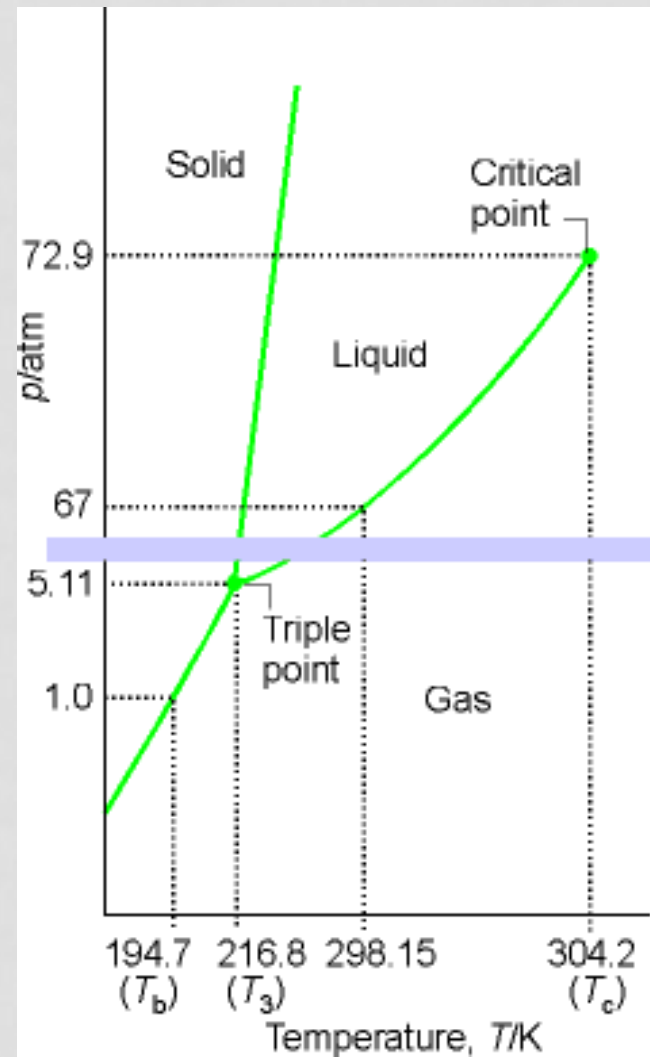
I. PHASE DIAGRAMS

- Experimentally defined diagrams. They reflect equilibrium states.
 - Areas: only one phase is stable (gas laws apply within such an area).
 - Lines (phase boundaries): two phases are stable, they are in equilibrium.
- Triple point (T_3): three phases are stable in equilibrium.
- Critical point (T_c): at temperatures higher than T_c , there is the gas phase, at lower temperatures, the vapor phase.
- Supercritical state



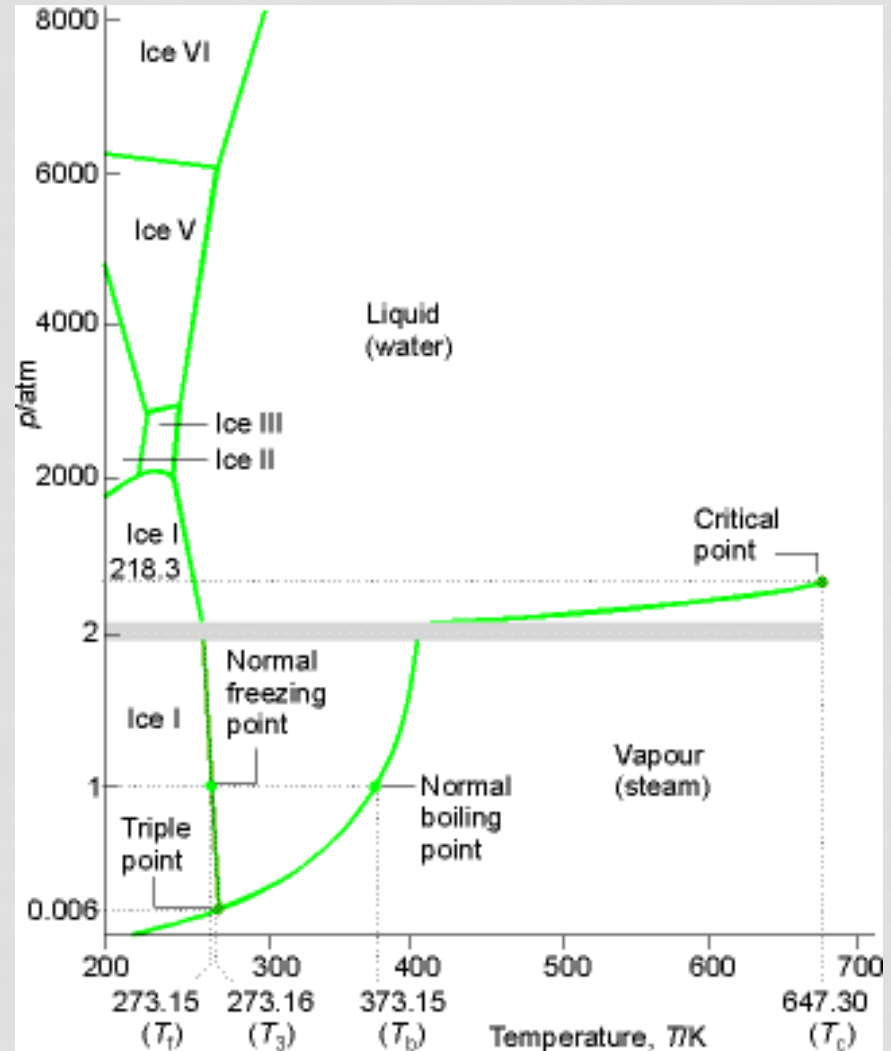
I. PHASE DIAGRAMS

- Phase diagram of CO₂:
 - Since the triple point is above 1 atm, the fluid does not exist at atmospheric pressure.
 - In a CO₂ gas cylinder, there is liquid or high-pressure gas.
 - Solid CO₂ sublimates so it is called "dry ice".



I. PHASE DIAGRAMS

- Phase diagram of H_2O :
 - The melting point of ice **decreases** with increasing pressure! (The density of $\text{H}_2\text{O}(l)$ is higher and molar volume is lower than for ice.)
 - At high pressures, there are different crystalline forms of ice (II, III, V, VI, VII).



II. PHASE STABILITY AND PHASE TRANSITIONS

Experience:

- These are **physical** (not chemical) transitions.

	→ name	← name	Comment
$l \leftrightarrow g$	evaporation	condensation	Two types of boiling points: <ul style="list-style-type: none"> • <i>normal</i>: 1 atm • <i>standard</i>: 1 bar
$s \leftrightarrow l$	melting	freezing	Two types of melting/freezing points: <ul style="list-style-type: none"> • <i>normal</i>: 1 atm • <i>standard</i>: 1 bar
$s \leftrightarrow g$	sublimation	condensation	
$s_\alpha \leftrightarrow s_\beta$	solid phase transitions		usually slow

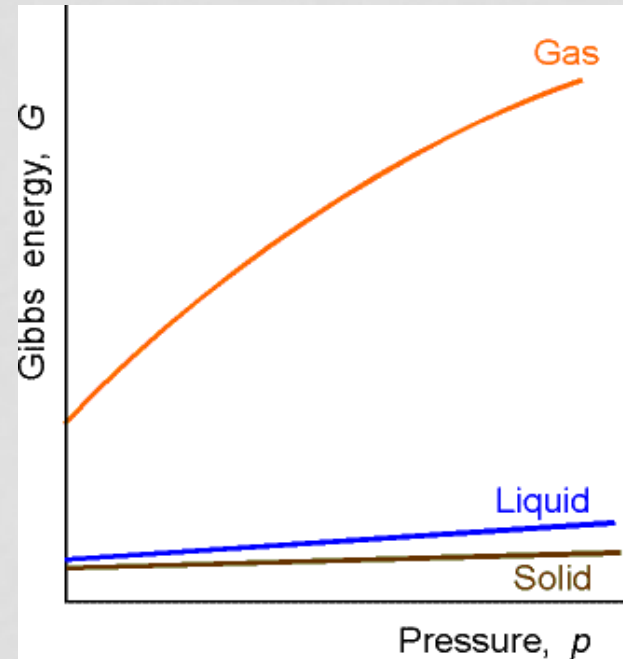
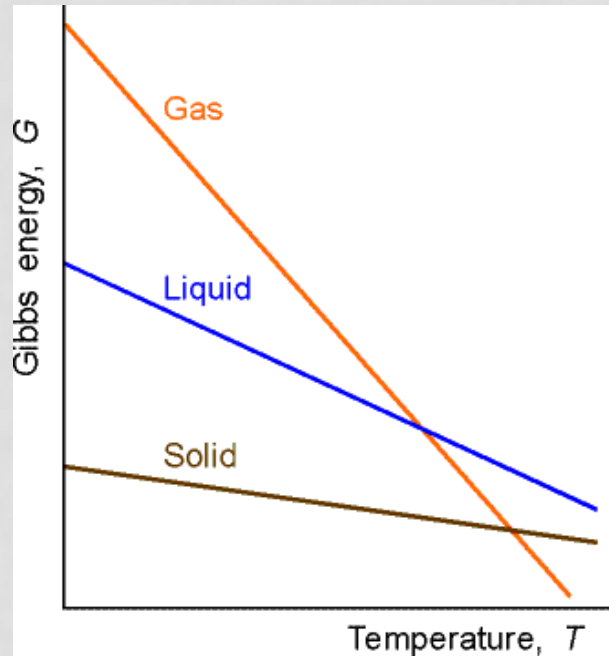
III. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

- Look at a system with constant p and T , where μ is not the same in all phases, *i.e.* there is equilibrium in the system.
- If $\mu_1 > \mu_2$, than dn amount of substance is transferred from state 1 to state 2 (this can be either physical or chemical transformation).

Initial state	Spontaneous process	Final state
$\mu_1 > \mu_2$	$\mu_1 \xrightarrow{dn} \mu_2$ $- \mu_1 dn \quad + \mu_2 dn$ $dG = (\mu_2 - \mu_1) dn < 0$	$\mu_1 = \mu_2$ $dG = 0$

III. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

- It is well-known how the chemical potential changes with changing the conditions (T, p):



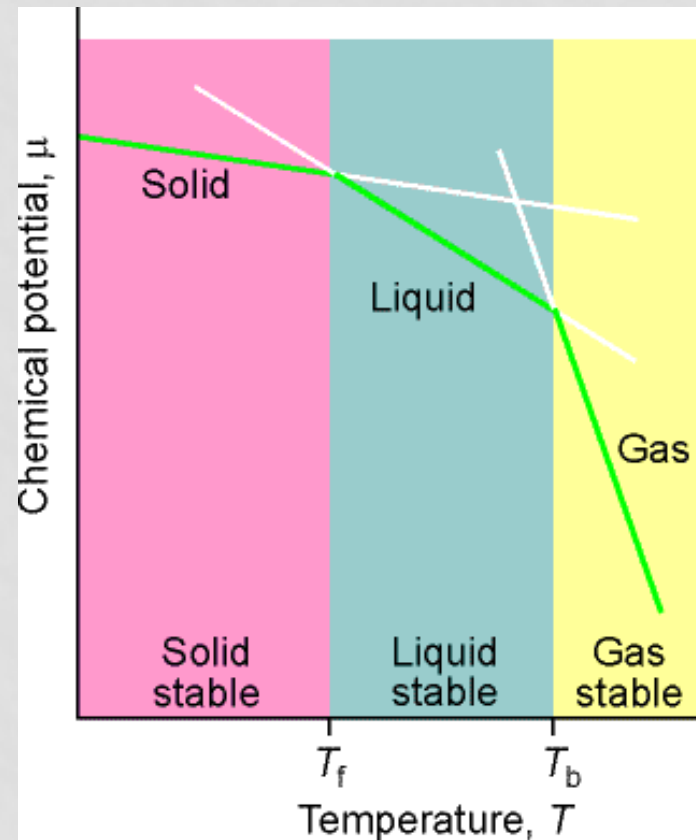
$$-S = \left(\frac{\partial G}{\partial T} \right)_p \longrightarrow -S_m = \left(\frac{\partial \mu}{\partial T} \right)_p$$

$$V = \left(\frac{\partial G}{\partial p} \right)_T \longrightarrow V_m = \left(\frac{\partial \mu}{\partial p} \right)_T$$

III. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

Summarizing the T -dependence of the different states:

- the μ chemical potential decreases with increasing T . The slope increases in the solid \rightarrow liquid \rightarrow gas direction (since the entropy of the system increases in this order).
- When changing T and p , phase transitions occur (forth and back).
- Phase transitions occur at well-defined temperatures and depend on the pressure p .



IV. EFFECT OF PRESSURE ON PHASE EQUILIBRIA

The effect of p external pressure to the T_{fus} melting point:

- It is known from thermodynamics that the μ chemical potential increases with increasing p :

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V_m \quad \text{e.g. } d\mu = V_m dp$$

- Usually $V_m(l) > V_m(s)$, thus T_{fus} increases with increasing p : at higher pressures, the melting point of a solid is higher.
- **Water is an exception:** $V_m(l) > V_m(s)$, therefore, the T_{fus} melting point value decreases with increasing pressure. *(In everyday life: glaciers, skating)*

IV. EFFECT OF PRESSURE ON PHASE EQUILIBRIA

The effect of P external pressure to the p vapor pressure:

- Only the condensed (liquid) phase is affected by P .
- Experimental finding: ΔP external pressure increases the p vapor pressure because the molecules are "squeezed" into the vapor phase.
- Explanation: Initially, the chemical potential is the same in the two phases: $\mu(g)^* = \mu(l)^*$
- After ΔP change in the external pressure, the chemical potentials are still the same:
 $d\mu(g) = d\mu(l)$, $d\mu(g) = V_m(g)dp$ so $d\mu(l) = V_m(l)dP$.
- For a perfect gas: $V_m(g) = RT/p$ i.e. $d\mu(g) = RTdp/p$.
- From integration
(p^* is the normal vapor pressure): $p = p^* e^{\left(\frac{V_m(l)\Delta P}{RT}\right)}$

V. EFFECT OF TEMPERATURE ON VAPOR PRESSURE.

CLAPEYRON EQUATION.

- The two phases are in equilibrium: $\mu_\alpha(p, T) = \mu_\beta(p, T)$, and remain in equilibrium: $d\mu_\alpha = d\mu_\beta$
- From thermodynamics, $d\mu = V_m dp - S_m dT$ for both phases, so: $V_{\alpha,m} dp - S_{\alpha,m} dT = V_{\beta,m} dp - S_{\beta,m} dT$.
- Rearrangement of the equations gives the so-called **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

ΔS_m : molar entropy change for phase transition

ΔV_m : molar volume change for phase transition

- Three cases are discussed:
 - a) solid \rightarrow liquid,
 - b) liquid \rightarrow gas,
 - c) solid \rightarrow gas.

V. EFFECT OF TEMPERATURE ON VAPOR PRESSURE.

CLAPEYRON EQUATION.

a) solid \rightarrow liquid ($s \rightarrow l$) phase transition: **melting**

- The **Clapeyron equation** for melting/freezing:

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V \cdot T} \qquad dp = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \frac{dT}{T}$$

- $\Delta_{\text{fus}} H$ is always positive,
- $\Delta_{\text{fus}} V$ is usually positive (**except for water**), but also small, so, dp/dT is large and positive.
- Integration between p^* and p , and T^* and T (at constant $\Delta_{\text{fus}} H$ and $\Delta_{\text{fus}} V$):

$$p = p^* + \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \ln \frac{T}{T^*}$$
- Simplification and re-arrangement:

$$p = p^* + \frac{\Delta_{\text{fus}} H(T - T^*)}{\Delta_{\text{fus}} V \cdot T^*}$$
- This is the equation of the straight line on the phase diagram.

VI. CLAUSIUS-CLAPEYRON EQUATION

b) liquid \rightarrow vapor ($l \rightarrow g$) phase transition: **evaporation**

- The **Clapeyron equation** for evaporation/condensation:

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} S}{\Delta_{\text{vap}} V} = \frac{\Delta_{\text{vap}} H}{\Delta_{\text{vap}} V \cdot T}$$

- $\Delta_{\text{vap}} H$ is always positive,
- $\Delta_{\text{vap}} V$ is always large positive (even for water!), so, dp/dT is positive but smaller than for $s \rightarrow l$. At the same time, $\Delta_{\text{vap}} V \approx V_m(g)$.
- For a perfect gas: $V_m(g) = RT/p$.
- Summarizing these gives the **Clausius-Clapeyron equation**:
- Integrated form:

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

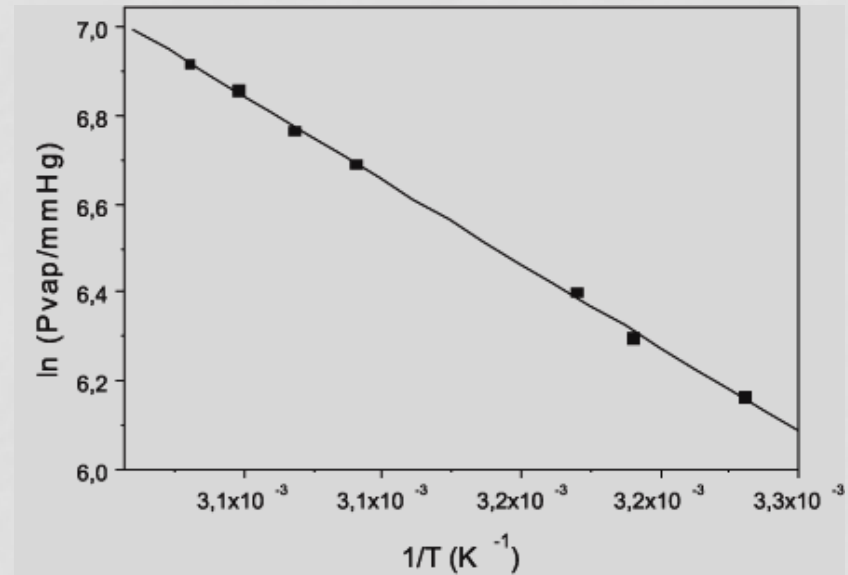
$$p = p^* e^{-\left[\frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right]}$$

VI. CLAUSIUS-CLAPEYRON EQUATION

- For two measured (p, T) pairs, definite integral gives the value of $\Delta_{\text{vap}}H$ as follows:

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

- A better solution is to measure many (p, T) data pairs. $\ln p$ plotted versus $1/T$ gives a straight line with a slope of $-\Delta_{\text{vap}}H/R$.



VI. CLAUSIUS-CLAPEYRON EQUATION

c) solid \rightarrow vapor (s \rightarrow g) phase transition: **sublimation**

- Sublimation is very similar to evaporation.
- Clausius–Clapeyron equation for sublimation:

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{sub}} H}{RT^2}$$

- Integrated form: $p = p^* e^{-\left[\frac{\Delta_{\text{sub}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right]}$

- For two measured (p, T) pairs, definite integral gives the value of $\Delta_{\text{vap}} H$ as follows:

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

VII. EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS

First-order phase transitions:

- the first derivative of chemical potential with respect to temperature ($d\mu/dT$) is discontinuous
 - e.g. $g \rightarrow l, l \rightarrow s, s \rightarrow g, \dots$

Second-order phase transitions:

- $\Delta H = 0, \Delta S = 0, \Delta V = 0$
- $d\mu/dT$ is continuous, but $d^2\mu/dT^2$ is discontinuous!
 - e.g. *conducting-superconducting transition in metals, order-disorder transitions in alloys, fluid-superfluid transition for He*



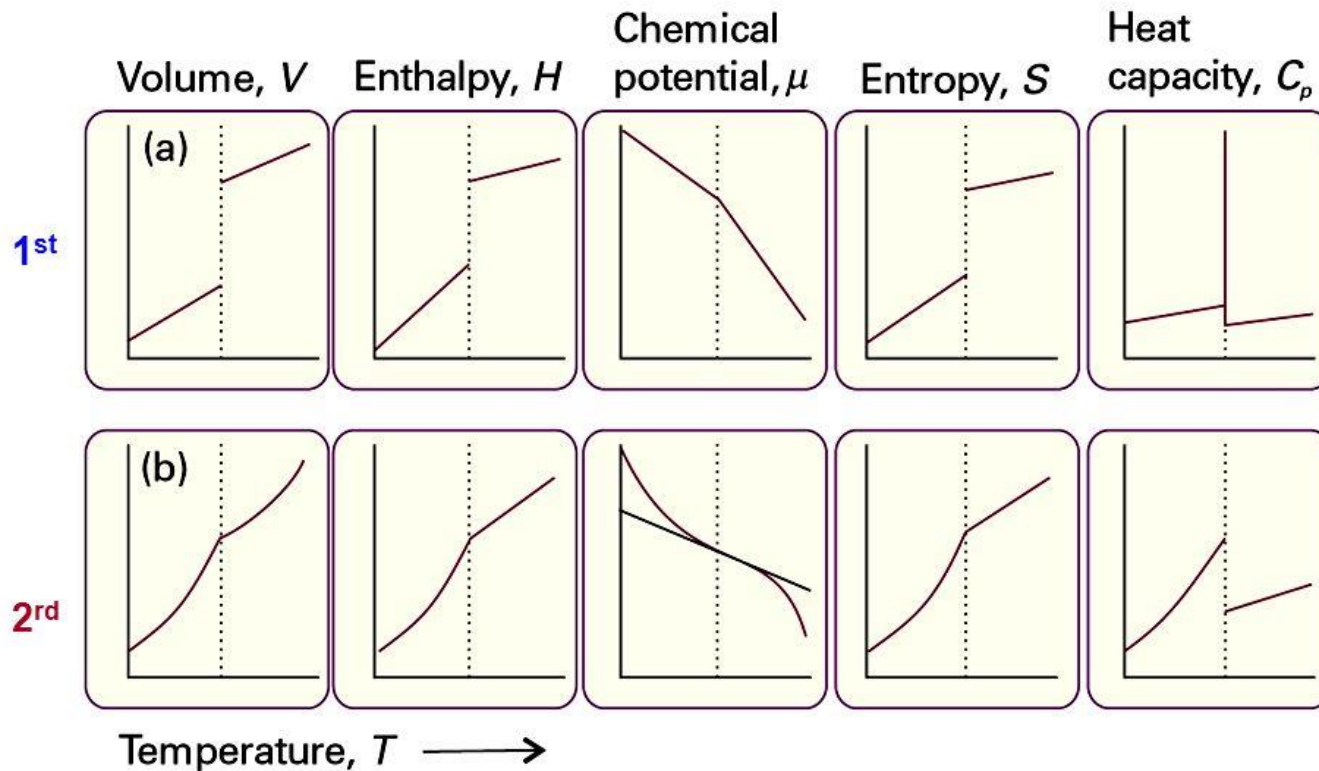
Paul Ehrenfest

1880 – 1933

Austrian and Dutch
theoretical physicist

VII. EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS

- Changes in thermodynamic properties accompanying phase transitions:



VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

- Liquids have a tendency to assume a shape that minimizes the surface → spherical **drops**
- **Reason:**
 - The work d_w necessary to increase the surface by $d\sigma$ is calculated as: $d_w = \gamma d\sigma$
(γ : surface tension, $\text{J m}^{-2} \equiv \text{N m}^{-1}$)
 - At constant T and V
 $d_w = dA = \gamma d\sigma$, and because $dA < 0$ then $d\sigma < 0$.



VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

- **Bubble:** a region filled with vapor (and air) enclosed within a thin liquid film.

double surface!



- **Cavity:** a region filled with vapor within a liquid.



Drop:



VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

Surface Tension of some Liquids

Table 2.1: Surface tensions γ of some liquids at different temperatures T .

Substance	T	γ (mNm^{-1})	Substance	T	γ (mNm^{-1})
Water	10°C	74.23	Mercury	25°C	485.48
	25°C	71.99		50°C	38.20
	50°C	67.94		25°C	28.22
	75°C	63.57		25°C	27.93
	100°C	58.91		25°C	27.20
Argon	90 K	11.90	<i>n</i> -pentane	25°C	15.49
Methanol	25°C	22.07	<i>n</i> -hexane	25°C	17.89
Ethanol	10°C	23.22	<i>n</i> -heptane	25°C	19.65
	25°C	21.97	<i>n</i> -octane	10°C	22.57
	50°C	19.89	25°C	21.14	
1-propanol	25°C	23.32	50°C	18.77	
1-butanol	25°C	24.93	75°C	16.39	
2-butanol	25°C	22.54	100°C	14.01	
Acetone	25°C	23.46	Formamide	25°C	57.03

VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

Laplace equation (for cavities): $p_{in} = p_{out} + \frac{2\gamma}{r}$

- The pressure is always larger in the internal part of a curved surface (on the concave side of the surface, within the cavity) than outside.

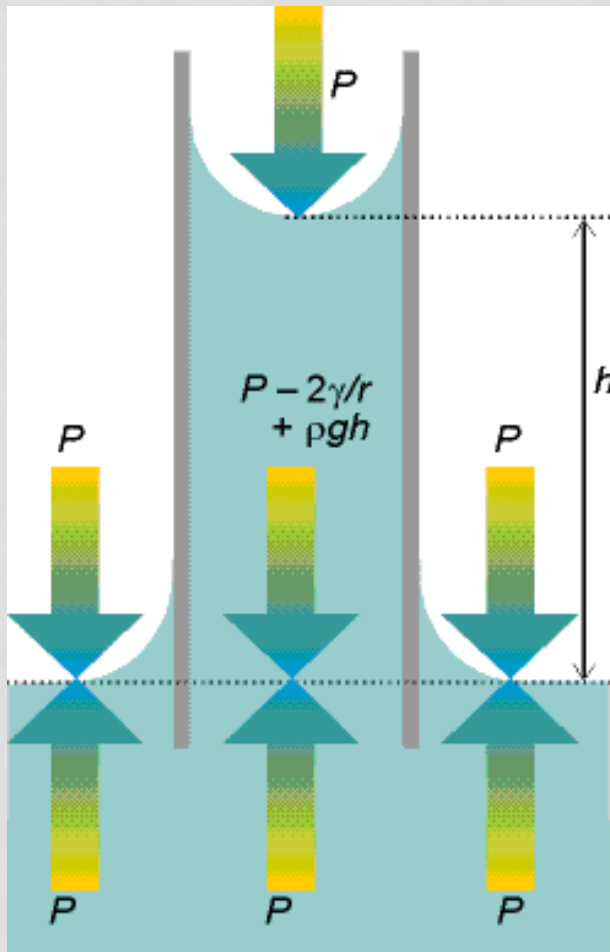
Kelvin equation (for droplets):

- the vapor pressure of a liquid depends on the external pressure:

$$p = p^* e^{\left(\frac{V_m(l)\Delta P}{RT}\right)} = p^* e^{\left(\frac{2\gamma V_m}{RT r}\right)}$$

VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

Laplace equation (for cavities): $p_{in} = p_{out} + \frac{2\gamma}{r}$



$$\frac{2\gamma}{r} = \rho gh$$

$$h = \frac{2\gamma}{\rho gr}$$

Measuring surface tension:

- by measuring r (number of droplets),
- from capillary rise.

VIII. SURFACE TENSION. CURVED SURFACE. CAPILLARY ACTION.

- Rise of liquid level due to capillary action: $h = \frac{2\gamma}{\rho g r}$

wetting
(convex)

non-wetting
(concave)

