

## 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. Thermodynamic significance of activity. Standard state convention

1

## 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**.

2

## CHEMICAL POTENTIAL

- The **chemical potential** is [equivalent definitions]:
  - partial molar Gibbs free energy (at constant T and p),

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

- Gibbs free energy change as an effect of adding exactly **1 mol** substance to the system,
- change of G with changing composition.
- The condition of equilibrium in all systems: the chemical potentials of a component in each phase must be the same.

3

## CHEMICAL POTENTIAL

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

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

- The chemical potential  $\mu_i$  of component *i* in a mixture is the partial molar Gibbs free energy:

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

4

## CHEMICAL POTENTIAL

### Chemical potential under different conditions:

definition of $\mu_j$ with G: (isothermal isobaric)	$\mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{T,p,n'}$
definition of $\mu_j$ with U: (isochoric, isentropic)	$\mu_j = \left( \frac{\partial U}{\partial n_j} \right)_{V,S,n'}$
definition of $\mu_j$ with H: (isobaric, isentropic)	$\mu_j = \left( \frac{\partial H}{\partial n_j} \right)_{p,S,n'}$
definition of $\mu_j$ 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.

5

## I. CHEMICAL POTENTIAL OF AN IDEAL GAS

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

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

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

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

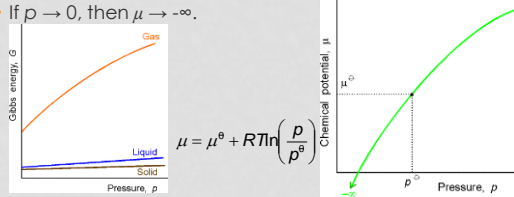
$$\mu = \mu^\ominus + RT \ln \left( \frac{p}{p^\ominus} \right)$$

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

6

### I. CHEMICAL POTENTIAL OF AN IDEAL GAS

- The chemical potential of an **ideal gas** depends linearly on  $\ln p$  and the proportionality factor is  $RT$ .
- The standard state is reached at  $p^\ominus$ .
- If  $p \rightarrow 0$ , then  $\mu \rightarrow -\infty$ .



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

7

### I. CHEMICAL POTENTIAL OF A REAL GAS

- Ideal thermodynamic relationships are often not useful with the measured  $p$  values.
  - E.g. in the  $A + B \rightleftharpoons C + D$  gas phase reaction, the equilibrium constant  $K = p_C p_D / (p_A p_B)$  is different at different pressures.
  - Chemical potential does not have the advantageous properties when  $p$  is used to calculate its value.
- There is a **p-like** property [its values can be collected in tables or graphs], which gives constant  $K$  values even at high pressures, so the TD equations containing  $K$  can still be used.
- The same is valid for other formulas containing  $p$ . This is the reason why **fugacity** was introduced.

8

### I. 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** ( $f$ ):

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

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

9

### I. CHEMICAL POTENTIAL OF A REAL GAS

- $RT \ln \gamma$  is a measure of the intermolecular forces. At low pressures, this decreases, so  $\gamma = 1$  when  $p = 0$ .

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

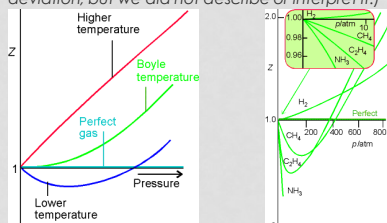
- $\gamma$  can be given using  $Z$  compression factor as follows:

$$\ln \gamma = \int_0^p \frac{Z-1}{p} dp$$

10

### I. CHEMICAL POTENTIAL OF A REAL GAS

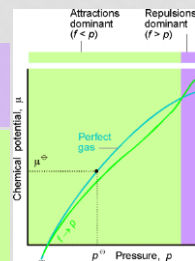
- Reminder:
  - $Z$  should be measured, but it is measurable quite well.
  - Plot  $Z$  as a function of pressure: sometimes larger, sometimes smaller, but if  $p \rightarrow 0$ , then  $Z \rightarrow 1$ . (We just showed the deviation, but we did not describe or interpret it.)



11

### I. CHEMICAL POTENTIAL OF A REAL GAS

- The reasons:
  - 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  $p \rightarrow 0$ ,  $\mu$  will be the same as for an ideal gas, as no significant intermolecular interaction is possible.



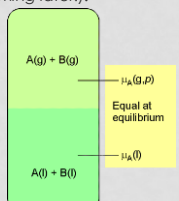
12

### III. CHEMICAL POTENTIAL OF LIQUIDS

- How does  $\mu$  depend on the composition?
- Starting point: in equilibrium,  $\mu$  is equal in the liquid and gas phases (*this is a general criterium for chemical equilibrium. More examples are coming later.*):

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

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



13

### 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 Gibbs free energies (chemical potentials) of the individual components:

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

- If only the compositions changes (constant  $T$  and  $p$ ):
- But from the definition:  $dG = \mu_A dn_A + \mu_B dn_B$
- Combining the two gives:

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

14

### IV. MULTICOMPONENT SYSTEMS. THE GIBBS-DUHEM EQUATION

- The general form for a multicomponent system, called the **Gibbs-Duhem equation**:

$$\sum n_j d\mu_j = 0$$

- Implication**: a change in the chemical potential of one of the components is necessarily accompanied by changes in the chemical potentials of the other components as well.

15

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

- For pure A ( $\cdot$ ):  $\mu_A^*(l) = \mu_A^*(g) = \mu_A^{\circ} + RT \ln \left( \frac{p_A^*}{p^{\circ}} \right)$
- A in solution:  $\mu_A(l) = \mu_A(g) = \mu_A^{\circ} + RT \ln \left( \frac{p_A}{p^{\circ}} \right)$
- 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):  $\mu_A(l) = \mu_A^*(l) + RT \ln(x_A)$

i.e. the chemical potential for a given substance in a mixture is proportional to the logarithm of its molar fraction.

16

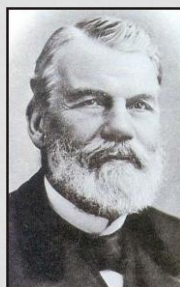
### V. IDEAL MIXTURES. RAOULT'S AND HENRY'S LAW

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

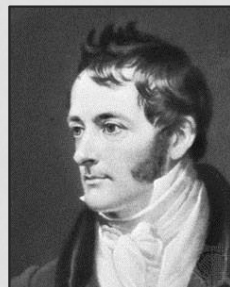
$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^*$$

- 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).

17



**François-Marie Raoult**  
1830 – 1901  
French chemist



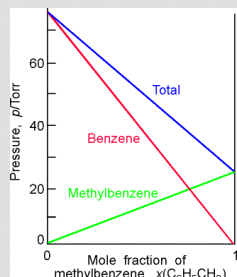
**William Henry**  
1774 – 1836  
English chemist

18

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

- The mixture of two similar liquids: total and partial molar pressures (**Raoult's law** valid)

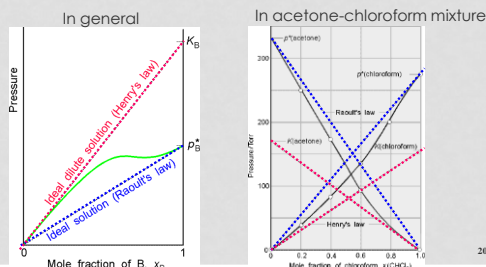
- E.g.: **Benzene + Toluene**
- Ethylbenzene + Styrene
- Hexane + Heptane
- Methanol + Ethanol



19

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

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



20

## 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 ( $\gamma$ ) are used instead of concentration.
- We will discuss:
  - the **activity of solvent A** (in molar fraction) and
  - the **activity of solute B** separately.
- An important question is the definition of the standard state. (For gases, it is simpler:  $p^\ominus$ )

21

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

### a) Activity of solvent A (in molar fraction)

- Chemical potential of solvent A in solution can be calculated from the vapour pressure of A above the solution:
 
$$\mu_A(l) = \mu_A^*(l) + RT \ln \left( \frac{p_A}{p_A^*} \right)$$
- For an **ideal mixture**, **Raoult's law** ( $p_A = x_A p_A^*$ ) stands for both (all) components, so:  $\mu_A(l) = \mu_A^*(l) + RT \ln x_A$
- Standard state for both the solvent and the solute is  $x_A = 1$  (pure liquid at 1 bar pressure).

- Real mixtures** does not follow Raoult's law but the formula can be kept when **a** is used instead of x:

$$\mu_A(l) = \mu_A^*(l) + RT \ln a_A$$

22

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

### a) Activity of solvent A (in molar fraction)

- Preferably:  $a_A = \gamma_A x_A$
- Logically,  $a_A \rightarrow x_A$  when  $x_A \rightarrow 1$   
 $\gamma_A \rightarrow 1$  when  $x_A \rightarrow 1$
- From this, the **chemical potential for solvent A** is:
 
$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$
- Standard state for solvent A**:  $x_A = 1$ , i.e. the pure liquid (l).
  - This is a real physical state.
  - Role of activity: "effective molar fraction"
  - Actual value of activity:  $a_A = p_A/p_A^*$ , so its value can be determined by vapor pressure measurements.

23

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

### b) Activity of solute B

- In an **ideal solution**, the molar fraction (concentration) of the solute is low ( $x_B \rightarrow 0$ ). This is very far from the pure solute ( $x_B \rightarrow 1$ ), so a different standard state should be chosen.
- Ideal dilute solutions** (**Henry's law**:  $p_B = x_B K_B$ )
- Chemical potential of solute B following **Henry's law**:
 
$$\begin{aligned} \mu_B &= \mu_B^\dagger + RT \ln(p_B/p_B^\dagger) = \mu_B^\dagger + RT \ln(K_B/p_B^\dagger) + RT \ln x_B = \\ &= \mu_B^\dagger + RT \ln x_B \end{aligned}$$

24

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

### b) Activity of solute B

- Real mixtures at higher concentrations usually do not follow Henry's law. To keep the formula for  $\mu$ , activity is used instead of molar fraction:

$$\mu_B = \mu_B^\dagger + RT \ln a_B = \mu_B^\dagger + RT \ln x_B + RT \ln \gamma_B$$

- The standard state is the same as for ideal mixtures. The difference from ideal mixtures is described by  $a_B$  and  $\gamma_B$ :

$$a_B = p_B/K_B = \gamma_B x_B$$

- When  $x_B \rightarrow 0$  (dilution),  $a_B \rightarrow x_B$  and  $\gamma_B \rightarrow 1$ .
- Real mixtures tend to be ideal when diluted.

25

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

### Molality-based activity:

- For mixtures (solutions), molality ( $m$ ) is often used instead of molar fraction. So, the use of molality-based activity is needed.
- In an ideal dilute solution for **solute B**,  $n_B \ll n_A$ , i.e.  $x_B \approx n_B/n_A$ .
- So:  $\mu_B = \mu_B^\dagger + RT \ln k + RT \ln(m_B/m^\ominus)$ .
  - [where  $x_B = k(m_B/m^\ominus)$ ,  $k$  is a dimensionless constant and  $m^\ominus = 1 \text{ mol kg}^{-1}$ .]
- Combining  $\mu_B^\dagger$  and  $RT \ln k$  gives:  $\mu_B = \mu_B^\ominus + RT \ln(m_B/m^\ominus)$ .
  - [where  $\mu_B^\ominus$  is the standard  $\mu$  of solute B when  $m_B = m^\ominus$ .]
- This gives:  $a_B = \gamma_B(m_B/m^\ominus)$ , where  $\gamma_B \rightarrow 1$  if  $m_B \rightarrow 0$ .
- in real solutions for **solute B**:  $\mu_B = \mu_B^\ominus + RT \ln a_B$ .

26

## VI. REAL MIXTURES AND SOLUTIONS: ACTIVITY

- Standard states (summary):

Component	Standard state	Chemical potential	Limits
solvent A <sup>†</sup> (Raoult's law)	pure solvent	$\mu_A = \mu_A^\ominus + RT \ln a_A$ $a_A = p_A/p_A^\ominus$ and $a_A = \gamma_A x_A$	$\gamma_A \rightarrow 1$ when $x_A \rightarrow 1$ (pure solvent)
solute B (Henry's law)	(1) pure solute (hypothetic state)	$\mu_B = \mu_B^\dagger + RT \ln a_B$ $a_B = p_B/K_B$ és $a_B = \gamma_B x_B$	$\gamma_B \rightarrow 1$ when $x_B \rightarrow 0$
	(2) $b^\ominus$ molality solute	$\mu_B = \mu_B^\ominus + RT \ln a_B$ $a_B = \gamma_B (b/b^\ominus)$	$\gamma_B \rightarrow 1$ when $b \rightarrow 0$

† The term includes the activity of pure liquids or solids:  $a = 1$ .  
The pressure is 1 bar in both cases.

27

## THERMODYNAMICS OF ONE-COMPONENT SYSTEMS

- Definition of phase and component
- Phase diagrams. Phase diagram of CO<sub>2</sub>, water and He.
- Phase stability and phase transitions
- The use of chemical potential to describe the equilibria in one-component multiphase systems
- The effect of pressure on phase equilibria
- The effect of temperature on phase equilibria. The Clapeyron equation.
- Liquid-vapor systems: Clausius–Clapeyron equation. Entropy of evaporation; Trouton's rule.
- Ehrenfest classification of phase transitions

28

## 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 ( $\mu$ ) 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.

29

## I. DEFINITION OF PHASE AND COMPONENT

- Definition of **phase**: a phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.
  - In a given phase, one or more components may be present (e.g. NH<sub>3</sub>, air).
- Definition of **component**: a chemically independent constituent (e.g. element, compound, ion) of a system.
  - A given component may be present in one or more phases of a system (e.g. H<sub>2</sub>O may be present in ice, water and water vapor if they are in equilibrium).

30

## I. DEFINITION OF PHASE AND COMPONENT

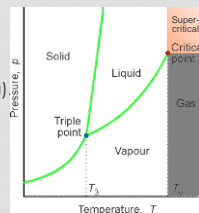
### Phases:

- Gaseous (vapor) state (g) (**gaseous phase**)
    - pure gases (1 component) or mixtures of gases (multi-component systems) – these can be described precisely.
  - Liquid state (l) (**liquid phase**)
    - pure liquid (1 component) or mixture of liquids or solution (2 or more components).
  - Solid state (s) (**solid phase**)
    - 1 component – in more than 1 structural forms: allotropes, e.g. for C, P, S, ice.
    - multicomponent systems: alloys, solid solutions, etc.
- [Plasma state: it is not common but important.]

31

## II. 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.

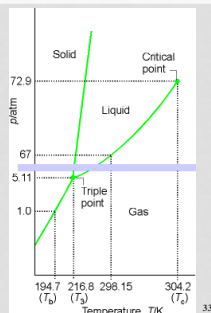


- Triple point ( $T_3$ ): three phases are stable in equilibrium.
- Critical point ( $T_c$ ): at temperatures higher than  $T_c$ , there is the gas phase, at lower temperatures, the vapor phase.
- Supercritical state

32

## II. PHASE DIAGRAMS

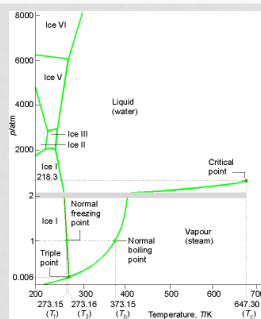
- Phase diagram of  $\text{CO}_2$ :
  - Since the triple point is above 1 atm, the fluid does not exist at atmospheric pressure.
  - In a  $\text{CO}_2$  gas cylinder, there is liquid or high-pressure gas.
  - Solid  $\text{CO}_2$  sublimates so it is called "dry ice".



33

## II. PHASE DIAGRAMS

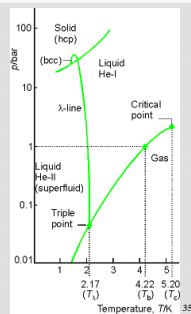
- Phase diagram of  $\text{H}_2\text{O}$ :
  - The melting point of ice **decreases** with increasing pressure! (The density of  $\text{H}_2\text{O}(l)$  is higher and molar volume is lower than for ice.)
  - At high pressures, there are different crystalline forms of ice (II, III, V, VI, VII).



[https://en.wikipedia.org/wiki/Category:273\\_Cradle](https://en.wikipedia.org/wiki/Category:273_Cradle)

## II. PHASE DIAGRAMS

- Phase diagram of  $^4\text{He}$ :
  - on the one hand, it reflects special behavior (liquid-liquid transition, superfluidity),
  - on the other hand, it is indispensable in the physics of low temperatures.



35

## III. 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"> <li>normal: 1 atm</li> <li>standard: 1 bar</li> </ul>
$s \leftrightarrow l$	melting	freezing	Two types of melting/freezing points: <ul style="list-style-type: none"> <li>normal: 1 atm</li> <li>standard: 1 bar</li> </ul>
$s \leftrightarrow g$	sublimation	condensation	
$s_\alpha \leftrightarrow s_\beta$	solid phase transitions		usually slow

36

### III. PHASE STABILITY AND PHASE TRANSITIONS

Phase transitions:

- In **equilibrium**, the chemical potential of a component is the same in the entire system (in all phases):
  - there is equilibrium inside a phase and
  - there is equilibrium between the phases.
- If that is not true, spontaneous processes will start in the system that will result in the equalization of chemical potentials.
- One of these processes is the phase transition (i.e. one phase transforms into another), which is a **physical change**.

37

### IV. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

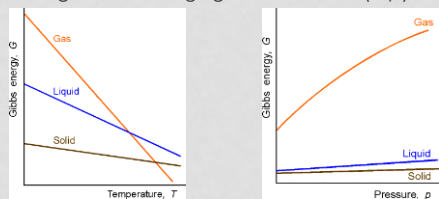
- Look at a system with constant  $p$  and  $T$ , where  $\mu$  is not the same in all phases, i.e. there is equilibrium in the system.
- If  $\mu_1 > \mu_2$ , then  $dn$  amount of substance is transferred from state 1 to state 2 (this can be either physical or chemical transformation).

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

38

### IV. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

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



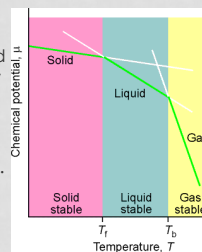
$$-S = \left( \frac{\partial G}{\partial T} \right)_p \longrightarrow -S_m = \left( \frac{\partial \mu}{\partial T} \right)_p \quad V = \left( \frac{\partial G}{\partial p} \right)_T \longrightarrow V_m = \left( \frac{\partial \mu}{\partial p} \right)_T$$

41

### IV. THE USE OF CHEMICAL POTENTIAL TO DESCRIBE PHASE TRANSITIONS

Summarizing the  $T$ -dependence of the different states:

- the  $\mu$  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  $p$ .



40

### V. 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  $\mu$  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)

41

### V. 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:**  $\Delta P$  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  $\Delta P$  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.  $d\mu(g) = RT dp/p$ .
- From integration ( $p^*$  is the normal vapor pressure):  $p = p^* e^{\left( \frac{V_m(l) \Delta P}{RT} \right)}$

### VI. 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**:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} \quad \Delta S_m: \text{molar entropy change for phase transition}$$

$$\Delta V_m: \text{molar volume change for phase transition}$$

- Three cases are discussed:

- solid  $\rightarrow$  liquid,
- liquid  $\rightarrow$  gas,
- solid  $\rightarrow$  gas.

43

### VI. EFFECT OF TEMPERATURE ON VAPOR PRESSURE. CLAPEYRON EQUATION.

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

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

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

- $\Delta_{fus} H$  is always positive,
- $\Delta_{fus} V$  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  $\Delta_{fus} H$  and  $\Delta_{fus} V$ ):

$$p = p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T}{T^*}$$

- Simplification and re-arrangement:

$$p = p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V} \frac{(T - T^*)}{T^*}$$

- This is the equation of the straight line on the phase diagram. 44

### VII. CLAUSIUS-CLAPEYRON EQUATION

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

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

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

- $\Delta_{vap} H$  is always positive,
- $\Delta_{vap} V$  is always large positive (even for water!), so,  $dp/dT$  is positive but smaller than for s  $\rightarrow$  l. At the same time,  $\Delta_{vap} V \approx V_m(g)$ .

- For a perfect gas:  $V_m(g) = RT/p$ .

- Summarizing these gives the

- Clausius-Clapeyron equation:**

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

- Integrated form:

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

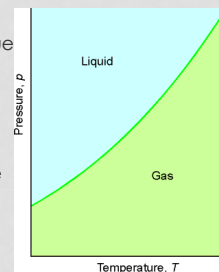
45

### VII. CLAUSIUS-CLAPEYRON EQUATION

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

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

- 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  $-\Delta_{vap} H/R$ .



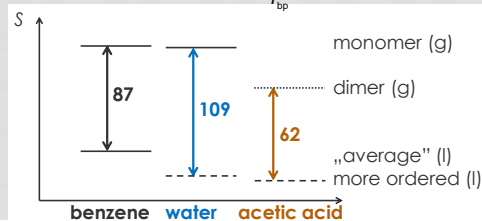
$$p = p^* e^{\left[ \frac{\Delta_{vap} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right]}$$

46

### VII. TROUTON'S RULE

- Trouton's rule:** most liquids have the same standard molar entropy of evaporation.

$$\frac{\Delta_{vap} H}{T_{bp}} = \Delta_{vap} S \approx 85 - 90 \text{ J mol}^{-1} \text{ K}^{-1}$$



47

### VII. CLAUSIUS-CLAPEYRON EQUATION

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

- Sublimation is very similar to evaporation.

- Clausius-Clapeyron equation for sublimation:

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

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

- For two measured ( $p, T$ ) pairs, definite integral gives the value of  $\Delta_{vap} H$  as follows:  $\ln \frac{p_2}{p_1} = -\frac{\Delta_{sub} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

48



### VIII. 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 transition and  $\lambda$ -transition:**

- $\Delta H = 0, \Delta S = 0, \Delta V = 0$
- $d\mu/dT$  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*

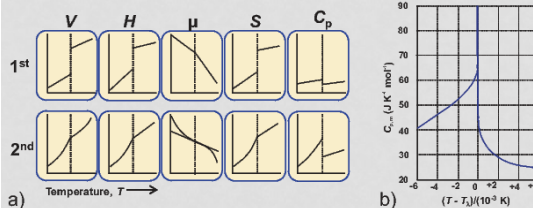


**Paul Ehrenfest**  
1880 – 1933  
Austrian and Dutch theoretical physicist

49

### VIII. EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS

- Changes in thermodynamic properties accompanying phase transitions:



50

### VIII. EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS

- The  $\lambda$ -curve for He, where the heat capacity rises to infinity. The shape of this curve is the origin of the name  $\lambda$ -transition.

