

2106NSC

Physical & Analytical Chemistry

Thermodynamics 6

Properties of real systems: Liquids, Phases

Liquids: Chemical potential

Consider a container in which there is a liquid in equilibrium with its vapour.

The chemical potential (Gibbs free energy) must be uniform throughout the system:

$$\mu_{(g)} = \mu_{(l)}$$

For an ideal gas, we know

$$\mu_{A(g)}^* = \mu_A^\ominus + R \cdot T \cdot \ln (p_{A}^*/p^\ominus) = \mu_{A(l)}^*$$

where the asterisks indicate the pure component (i.e. here the pure substance A).

Liquids: Chemical potential

Similarly, if there are two or more components in a liquid, for each component:

$$\mu_{A(l)} = \mu_{A(g)} = \mu_A^\ominus + R \cdot T \cdot \ln (p_A/p^\ominus)$$

Here, substance A is not pure, as it is in liquid state and in contact with another substance (hence no asterisk).

When we combine the two equations, we obtain:

$$\mu_{A(l)} - \mu_{A(l)}^* = \mu_{A(g)} - \mu_{A(g)}^* = R \cdot T \cdot \ln (p_A/p^\ominus) - R \cdot T \cdot \ln (p_A^*/p^\ominus)$$

$$\mu_{A(l)} = \mu_{A(l)}^* + R \cdot T \cdot \ln (p_A/p_A^*)$$

Raoult's Law

The derived equation

$$\mu_{A(l)} = \mu_{A(l)}^* + R \cdot T \cdot \ln (p_A/p_A^*)$$

can be transformed with some basic algebra to yield:

$$\frac{p_A}{p_A^*} = e^{-\frac{1}{R \cdot T} \frac{\mu_A}{\mu_A^*}} = x_A$$

If a system obeys **Raoult's law**, which is the case for ideal solutions, the pressure of A in the vapour is proportional to the amount of A in the liquid:

$$p_A = x_A \cdot p_A^*$$

The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.

Raoult's Law

The effect of Raoult's Law is that the saturated vapour pressure of a solution is going to be lower than that of the pure solvent at any particular temperature.

This has important effects on the phase diagram of the solvent.

[Chemistry LibreTexts: Raoult's Law](#)

Activity: Mole fraction for a non-ideal solution

$$\mu_{A(l)} = \mu_{A(l)}^* + R \cdot T \cdot \ln (p_A/p_A^*)$$

From Raoult's Law, it follows for an ideal ideal solution:

$$\mu_{A(l)} = \mu_{A(l)}^* + R \cdot T \cdot \ln x_A$$

In the same way that we defined fugacity (f) for a gas, we can define **activity** (a) for a solution.

We assume that the above equation is true for a real liquid when the mole fraction is replaced with activity.

So for a real solution

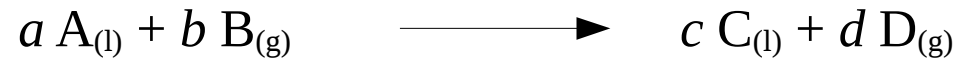
$$\mu_{A(l)} = \mu_{A(l)}^* + R \cdot T \cdot \ln a_A$$

The activity coefficient γ indicates the deviation from the ideal mole fraction

$$a_A = \gamma_A \cdot x_A$$

ΔG for a reaction

Consider the chemical reaction:



The change in free energy is given by

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} \quad \text{extensive (depends on the actual amounts)}$$

$$\Delta G = (c \cdot G_{mC} + d \cdot G_{mD}) - (a \cdot G_{mA} + b \cdot G_{mB})$$

$$\Delta G = (c \cdot \mu_C + d \cdot \mu_D) - (a \cdot \mu_A + b \cdot \mu_B)$$

$$\Delta G = (c \cdot \mu_C^* + c \cdot R \cdot T \cdot \ln x_C + d \cdot \mu_D^\emptyset + d \cdot R \cdot T \cdot \ln p_D) - (a \cdot \mu_A^* + a \cdot R \cdot T \cdot \ln x_A + b \cdot \mu_B^\emptyset + b \cdot R \cdot T \cdot \ln p_B)$$

$$\Delta G = \Delta G^\emptyset + R \cdot T \cdot \ln \frac{(x_C)^c \cdot (p_D)^d}{(x_A)^a \cdot (p_B)^b} = \Delta G^\emptyset + R \cdot T \cdot \ln Q \quad ; Q \text{ is the } \mathbf{\text{reaction coefficient}}$$

ΔG at equilibrium

We know that at equilibrium

$$\Delta G = 0$$

At equilibrium, the reaction coefficient Q is the equilibrium constant

$$Q_{eq} = K$$

Therefore at equilibrium:

$$\Delta G = \Delta G^\ominus + R \cdot T \cdot \ln K = 0$$

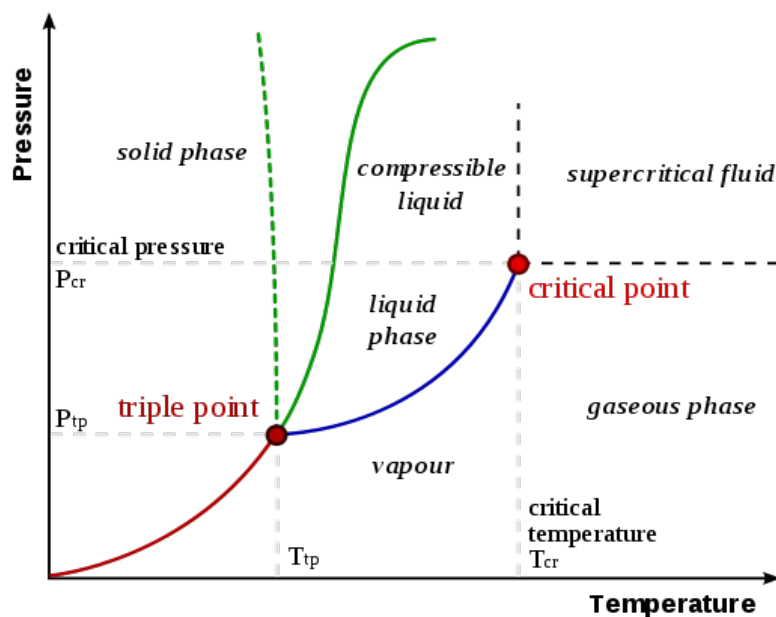
$$\Rightarrow \ln K = \frac{-\Delta G}{R \cdot T}$$

$$\Rightarrow K = e^{-\frac{\Delta G}{R \cdot T}}$$

If we can determine the free energy change of a process, we can work out the equilibrium constant.

Phase equilibria and colligative properties

Phase diagrams tell us the state of a system under various conditions. They are typically presented as p - T or p - V diagrams.

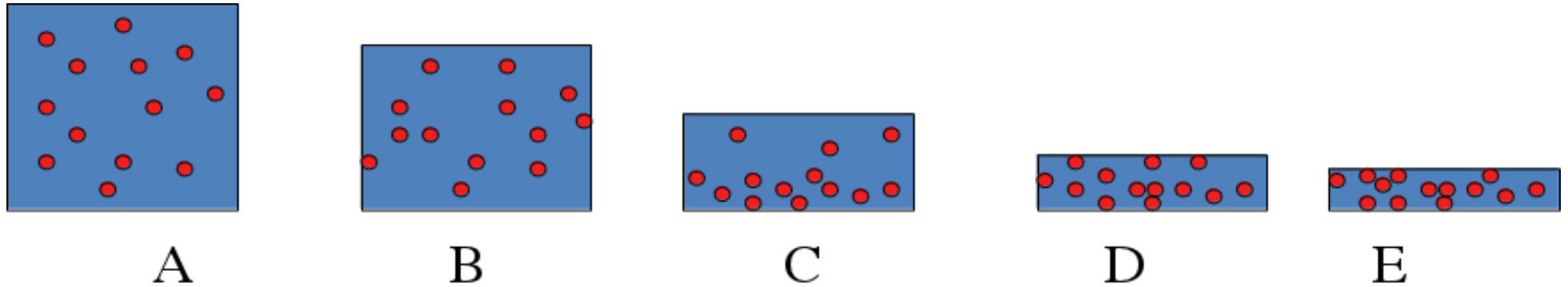


Chemistry LibreTexts:
Phase diagrams

Colligative properties

Properties of liquids (T_m , T_b , p_v , π) depend on the presence of solute molecules, i.e. the number of particles.

Condensation



The lines in the p - V diagram are called **isotherms**. The temperature is the same all the way along.

The dotted line in the p - V diagram on the next slide is the isotherm of an ideal gas.

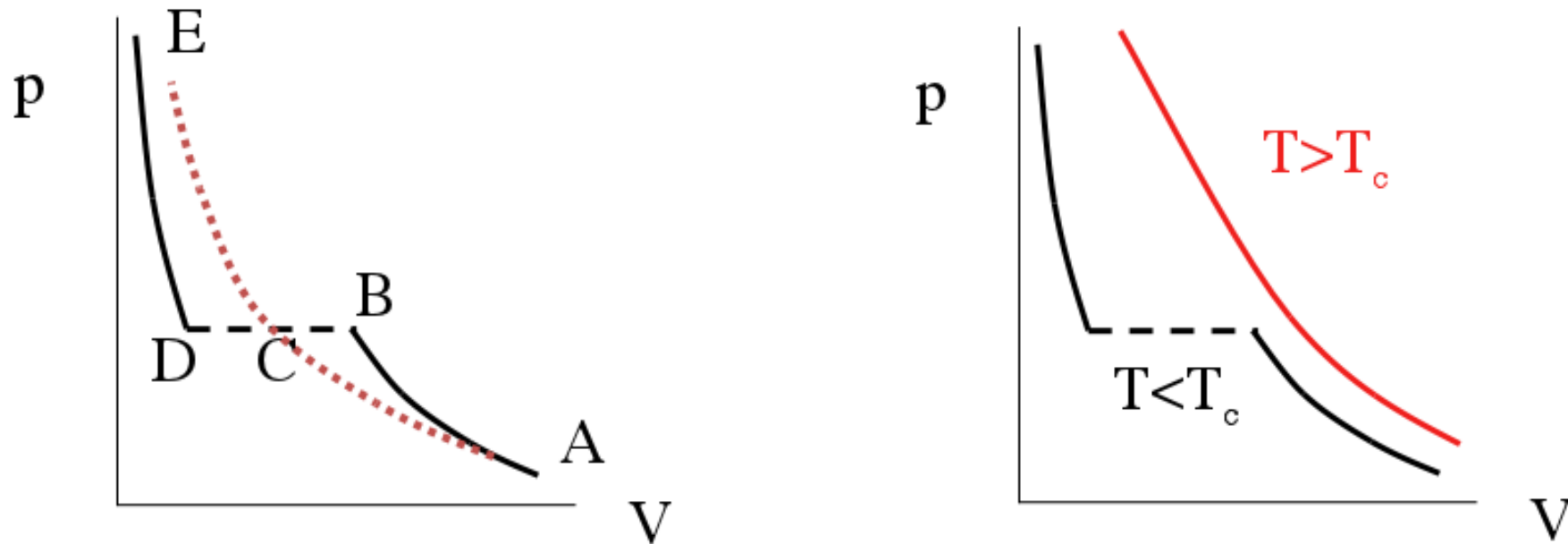
The black line is the isotherm for a real gas; it undergoes **condensation**. At a certain pressure, the volume collapses (B-C-D) and the gas turns into a liquid. The pressure at B-C-D is called the **vapour pressure** of the liquid.

Critical constants

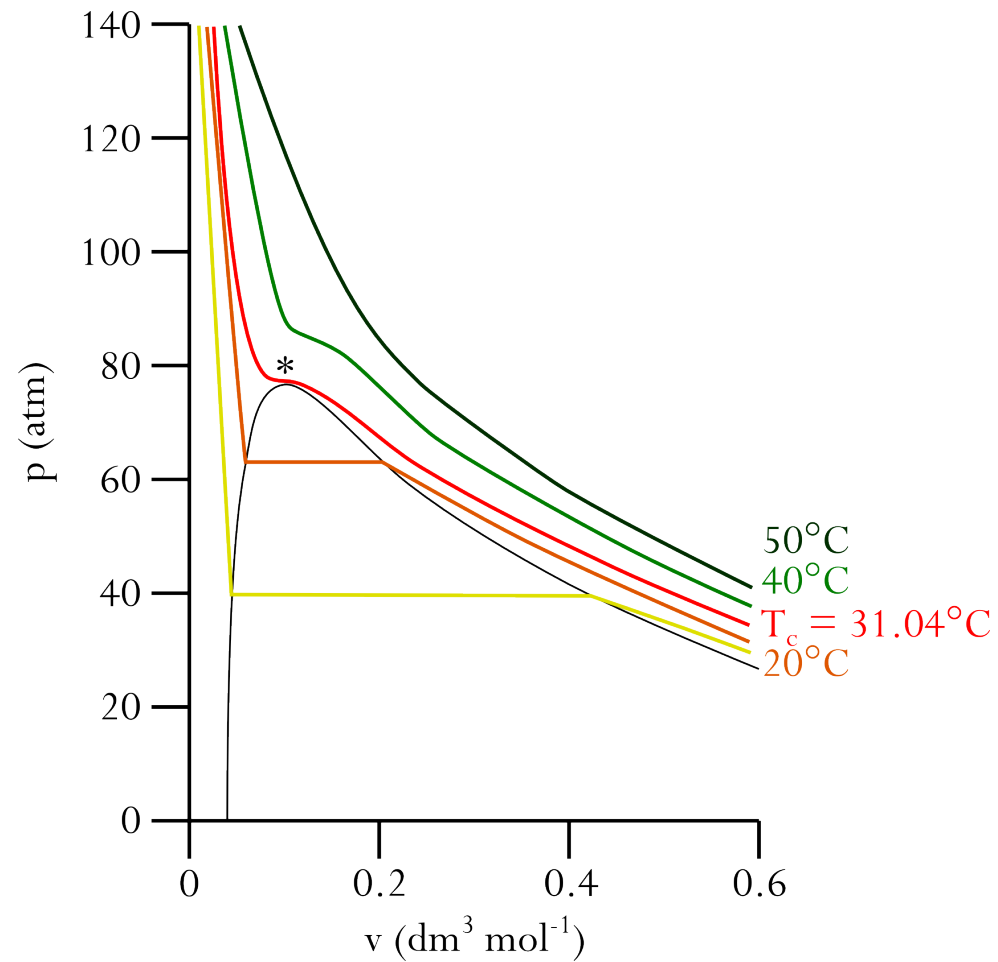
For condensation to occur, the molecules must be close enough and slow enough to aggregate.

High temperatures imply high molecular velocities.

At sufficiently high temperatures, no condensation will occur, no matter how small the volume is made - this is the **critical temperature** (T_c).



Critical constants



Isotherms of CO₂ at different temperatures. The critical point is marked with '*'.

Critical constants

The critical point is the point (with values of p_C , T_C and V_C) at which the critical isotherm has zero slope.

The critical point is a characteristic of a particular substance.

	p_C (atm)	V_C (cm ³ mol ⁻¹)	T_C (°C)
Ar	48.0	75.3	-123
CO₂	72.9	94.0	31.0
He	2.26	57.8	-268
O₂	50.1	78.0	-118

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.

Sections III.2.1-III.3.2

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.

Section 1.3 (pp. 30-32)

Sections 5.3-5.5 (pp. 164-176)