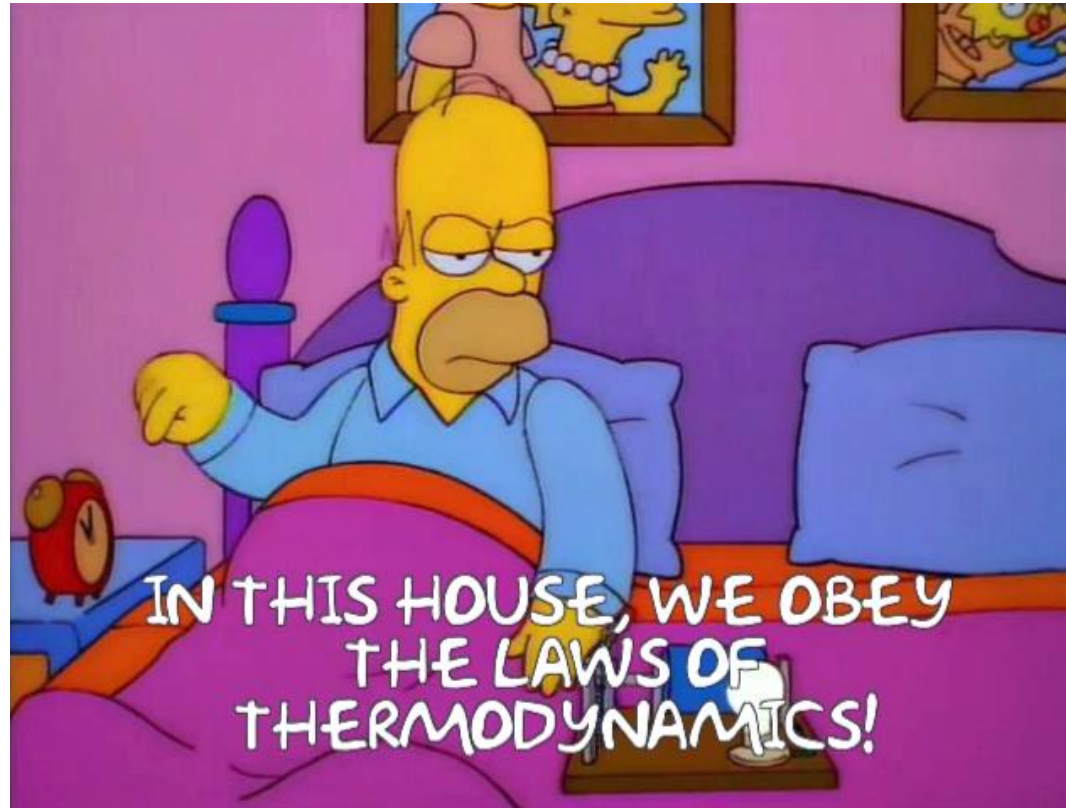


Thermodynamics (lecture 7)



Roel Dullens

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Summary lecture 6

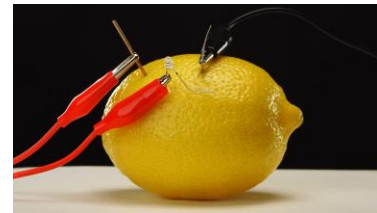
- Chemical equilibrium

- Van 't Hoff equation
- Change of composition with pressure

$$\left(\frac{\partial \ln K_p}{\partial T}\right) = \frac{\Delta_r H^\ominus}{RT^2}$$
$$K_p = \frac{16}{27} \left(\frac{1 - \alpha^2}{\alpha^2}\right)^2 \left(\frac{p^\ominus}{p}\right)^2 \quad (\text{example})$$

- Electrochemistry

- Electrochemical cells, half- and cell reactions
- Reaction Gibbs energy and cell potential
- Nernst equation
- Standard hydrogen electrode



$$\Delta_r G = -\nu F E_{\text{cell}}$$

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{\nu F} \ln Q$$

$$\text{Pt(s)}|\text{H}_2(\text{g})|\text{H}^+(\text{aq}) \quad E^\ominus = 0 \quad \text{at all } T$$

Content of the course

- ✓ Introduction to Thermodynamics and gases
- ✓ The First Law of Thermodynamics
- ✓ Heat Capacities, Enthalpy and Thermochemistry
- ✓ The Second Law of Thermodynamics
- ✓ Helmholtz and Gibbs free energies
- ✓ Phase Transitions and Chemical Equilibrium
- ✓ Chemical Equilibrium and Electrochemistry

- Ideal solutions, Colligative properties

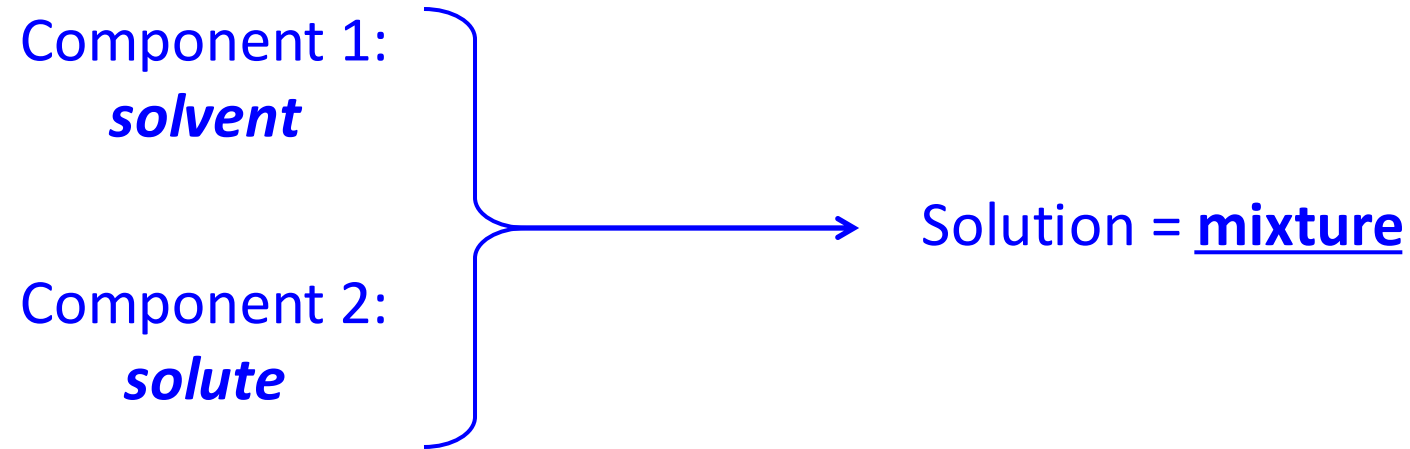
- Condensation in the Van der Waals equation of state

} Today, lecture 7

Today's lecture (7)

- Ideal solutions
 - Thermodynamics of mixing
- Colligative properties of ideal solutions
 - Vapour pressure: Raoult's law
 - Depression of freezing point (and elevation of boiling point)
 - Osmosis
- Beyond perfect gases: Van der Waals gas
 - Condensation and the critical point

Solutions: thermodynamics of mixing



From lecture 5:

Gibbs free energy:

$$G = G_{\text{unmixed}} + \Delta_{\text{mix}}G$$

Gibbs free energy of mixing

Enthalpy of mixing

with: $\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S$

Entropy of mixing

Thermodynamics of solutions

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S$$

model to find expressions
for $\Delta_{\text{mix}}S$ and $\Delta_{\text{mix}}H$

$$G = G_{\text{unmixed}} + \Delta_{\text{mix}}G$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$$

Condition for chemical equilibrium

$$\mu_i^\alpha = \mu_i^\beta$$

Colligative properties:

properties that depend on amount of solute particles

Recall from lecture 6:

Chemical potential in terms of *activities* a_i

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$

-
- Solutions

$$a_i = \gamma_i x_i$$

x_i : mole fraction (as seen before)

$\gamma_i = 1$ for ideal solutions (see lecture 7)

... so we already know the chemical potential for solutions ...

$$\mu_i = \mu_i^* + RT \ln x_i$$

Note different 'reference point' μ_i^*

In this lecture we will see a 'taster of statistical thermodynamics' to derive this

(recall: *classical thermo*: independent of molecular hypothesis & *stat. thermo*: based on molecular hypothesis)

Simplest model for solutions: ideal solutions

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S$$

model to find expressions
for $\Delta_{\text{mix}}S$ and $\Delta_{\text{mix}}H$

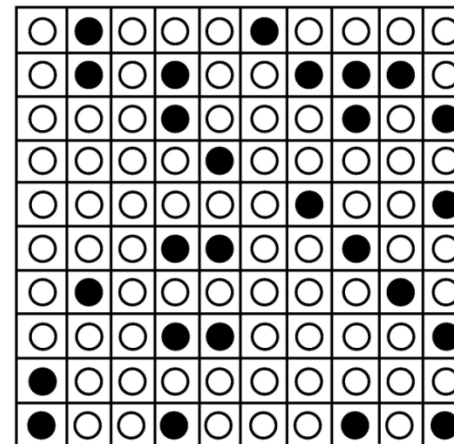
Enthalpy of mixing

$$\Delta_{\text{mix}}H = 0$$

all interactions are the same
(different from perfect gas!)

Ideal entropy of mixing

Lattice model of a binary mixture



N_1 molecules of type 1

N_2 molecules of type 2

$N = N_1 + N_2$ lattice sites

Random mixing

$$x_1 = \frac{N_1}{N_1 + N_2} \quad x_2 = \frac{N_2}{N_1 + N_2}$$

(note: here is the **statistical thermo bit**: based on particles)

Recall from lecture 3:

Statistical interpretation of entropy



Ludwig Boltzmann
(1844 – 1906)

$$S = k_B \ln W$$

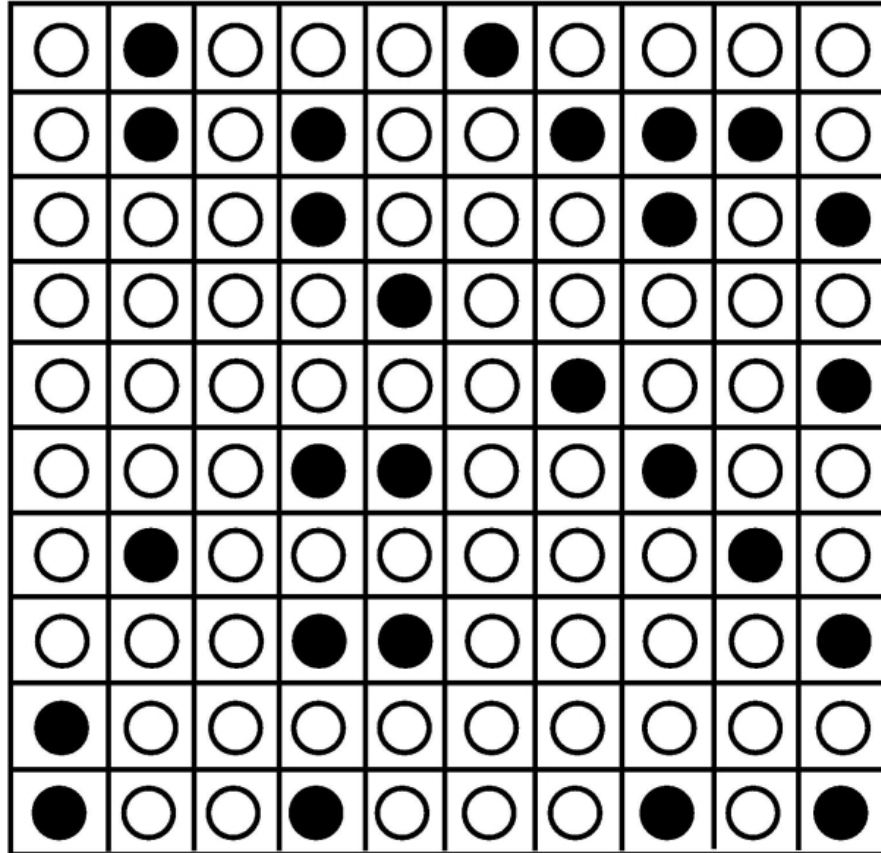
W : number of microstates associated with a macrostate



Number of ways in which you can realise a given configuration

Recall from lecture 3:

W : $N_1 + N_2$ molecules on N lattice sites



$$\Omega = \frac{N!}{N_1!N_2!}$$

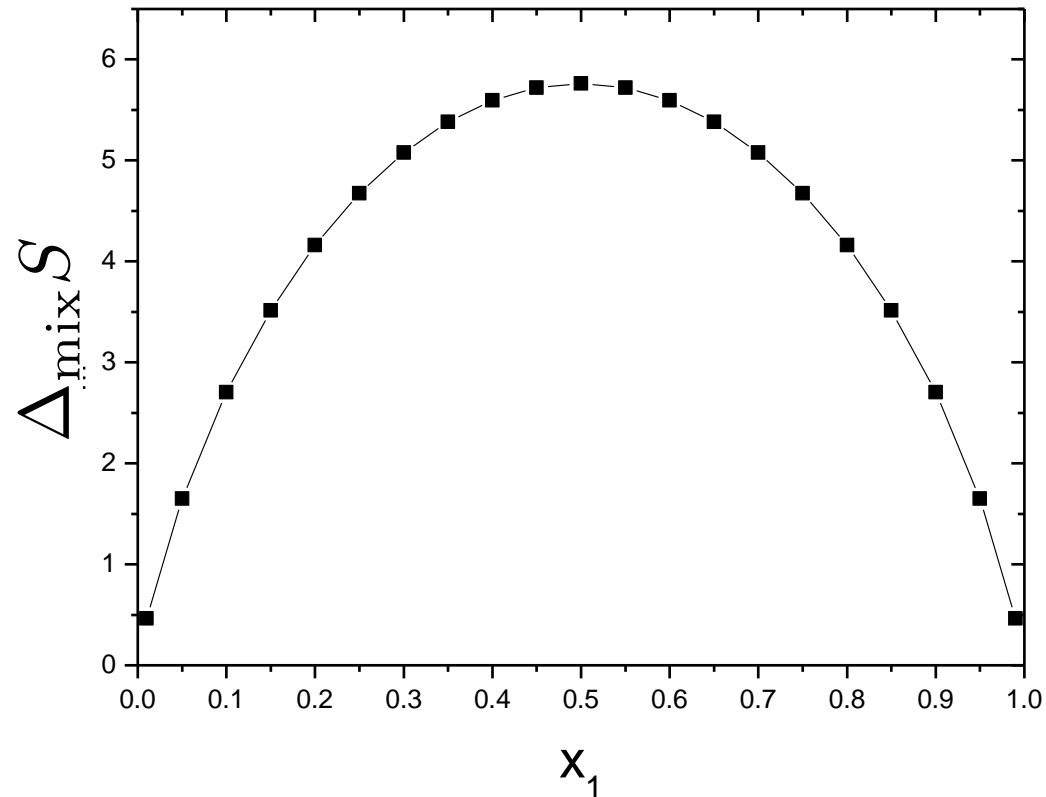
Combinatorics: see e.g. Molecular driving forces, Dill and Bromberg

Entropy of mixing for ideal solution

Recall from lecture 5:

$$\Delta_{\text{mix}}S = S_{\text{after mixing}} - S_{\text{before mixing}}$$

$$\Delta_{\text{mix}}S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$



Entropy, enthalpy and Gibbs energy of mixing (ideal)

Enthalpy of mixing

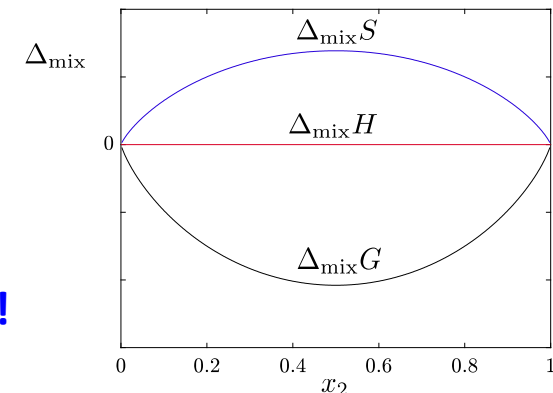
$$\Delta_{\text{mix}}H = 0$$

Ideal entropy of mixing

$$\Delta_m S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S$$

$$\Delta_{\text{mix}}G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$



Note: same expressions as for the mixing of perfect gases (lecture 5)!

Chemical potential of ideal solution

$$G = G_{\text{unmixed}} + \Delta_{\text{mix}}G$$

$$\Delta_{\text{mix}}G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$G = G_{\text{unmixed}} + nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$$

Exercise 32 (hint: express x_i in n_i)

$$\mu_i = \mu_i^* + RT \ln x_i$$

Today's lecture (7)

- Ideal solutions
 - Thermodynamics of mixing
- **Colligative properties of ideal solutions**
 - Vapour pressure: Raoult's law
 - Depression of freezing point (and elevation of boiling point)
 - Osmosis
- Beyond perfect gases: Van der Waals gas
 - Condensation and the critical point

Colligative properties of ideal solutions

Colligative properties: physical properties that depends on concentration of solute particles (not their identity)

- Vapour pressure
- Depression of freezing point
- Osmotic pressure



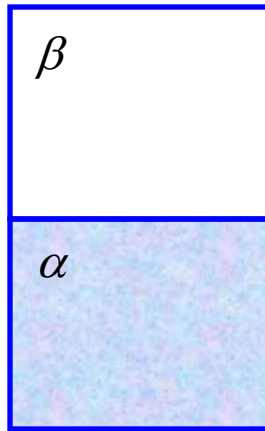
Chemical equilibrium of solutions

$$\mu_i^\alpha = \mu_i^\beta$$

Chemical potential of ideal solutions

$$\mu_i = \mu_i^* + RT \ln x_i$$

Vapour pressure of ideal solution (Raoult's law)

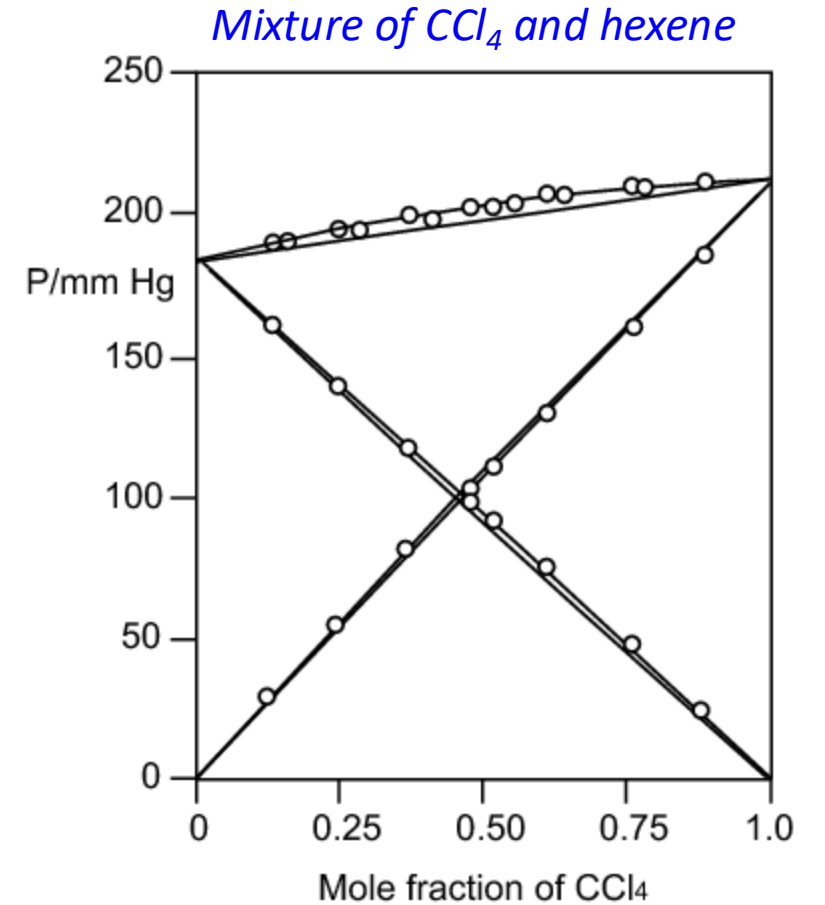


Perfect gas (mixture)

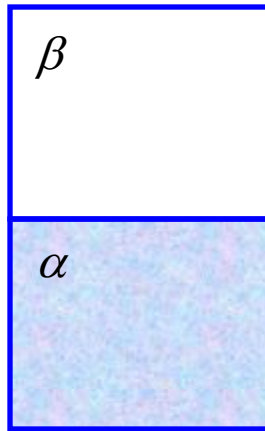
Ideal solution

$$\mu_i^\alpha = \mu_i^\beta$$
$$\mu_i^{\text{solution}} = \mu_i^{\text{vapour}}$$

$$p_i = x_i p_i^*$$



Depression of freezing point



Ideal solution

ideal solution
(water and alcohol)

(pure) solid (solvent)

solid solvent (ice)



$$\mu_1^\alpha = \mu_1^\beta$$
$$\mu_1^{\text{solid}} = \mu_1^{\text{solution}}$$

$$\Delta T = T - T^* = -x_2 \frac{RT^{*2}}{\Delta_{\text{fus}}H}$$

T^* : freezing point of water

x_2 : mole fraction of solute (e.g. alcohol)

Depression of freezing point and James Bond



Jökulsárlón, Iceland

Freezing Jökulsárlón?

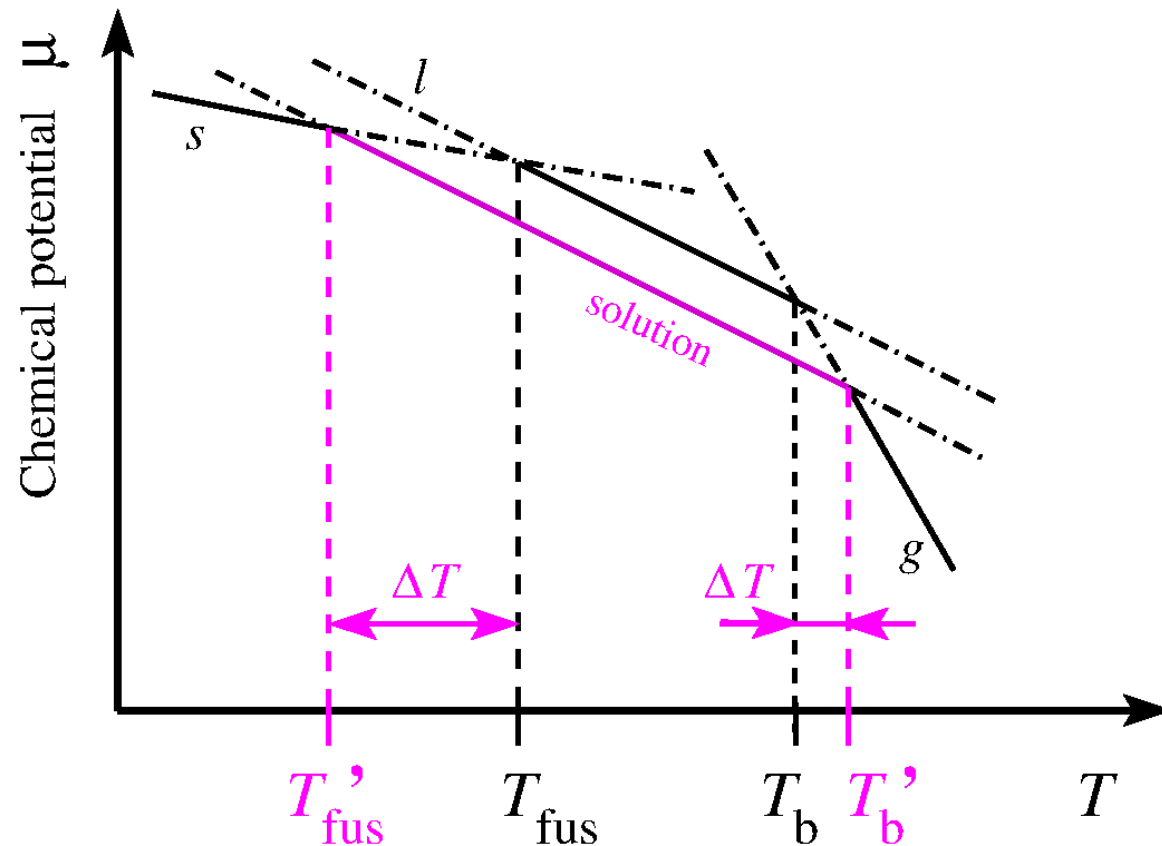


Freezing Jökulsárlón?



Depression of freezing and elevation of boiling point

$$\mu_1 = \mu_1^* + RT \ln x_1$$



Depression of freezing point

$$\Delta T = -x_2 \frac{RT^{*2}}{\Delta_{\text{fus}}H}$$

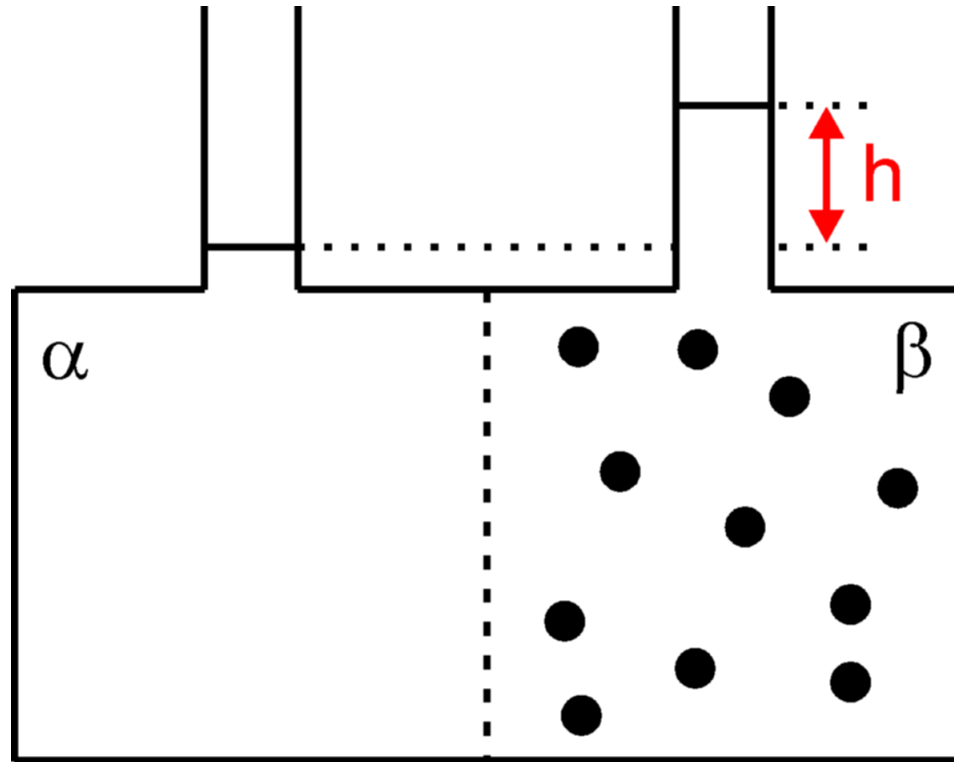
Elevation of boiling point

$$\Delta T = x_2 \frac{RT^{*2}}{\Delta_{\text{vap}}H}$$

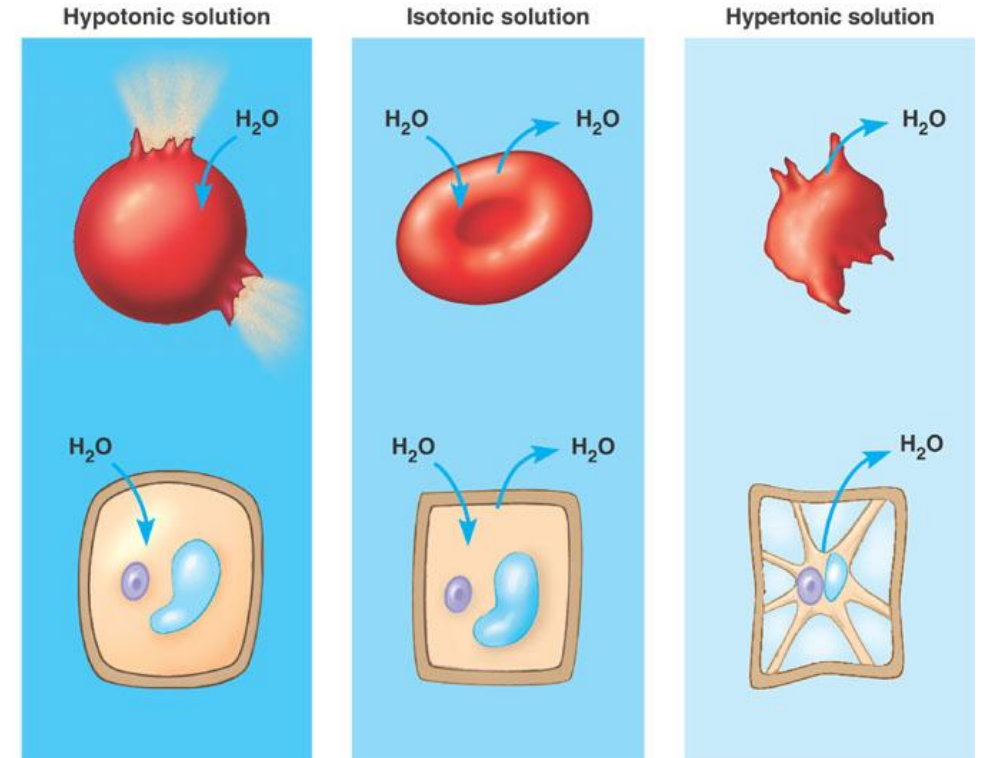
Today's lecture (7)

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 - **Osmosis**
- Beyond perfect gases: Van der Waals gas
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Osmotic pressure of ideal solutions

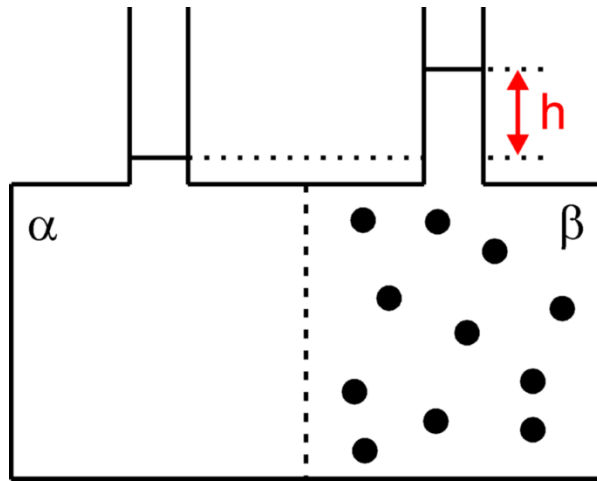


$$\Pi = p^{\beta} - p^{\alpha}$$



Osmosis: crucially important in biology

Osmosis: driven by $\mu = \mu$!



$$\Pi = P^\beta - P^\alpha$$

$$\Pi = \frac{\mu_1 - \mu_1^*}{V_{1,m}}$$

Still completely general!!!



Jacobus H. van 't Hoff
1852 - 1911

Osmotic pressure for ideal solutions?

Sub in: $\mu_1 = \mu_1^* + RT \ln x_1$

$$\Pi = [B]RT$$

Ideal osmotic pressure
(Van 't Hoff's equation)

(Yes I know, another one ...)

Osmosis in the kitchen

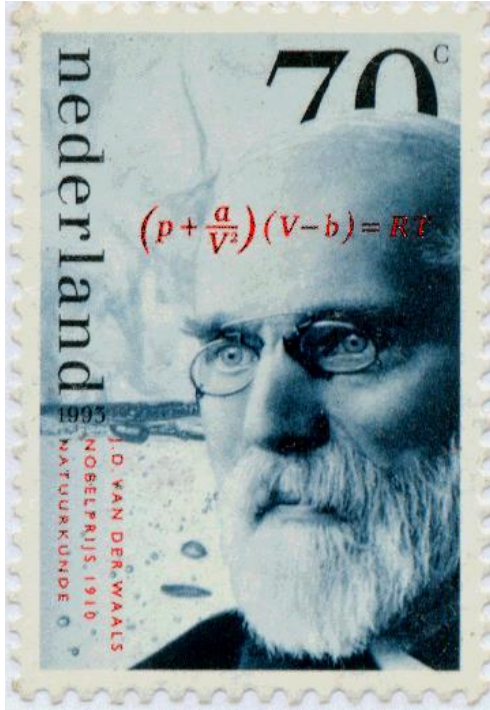
<https://youtu.be/H6N1liJTmnc>

Today's lecture (7)

- Ideal solutions
 - Thermodynamics of mixing
- Colligative properties of ideal solutions
 - Vapour pressure: Raoult's law
 - Depression of freezing point (and elevation of boiling point)
 - Osmosis
- **Beyond perfect gases: Van der Waals gas**
 - Condensation and the critical point

Recall from lecture 1:

Van der Waals Equation of State



Johannes Diderik Van der Waals
(1837 – 1923)

Over de continuïteit van den
gas – en vloeistof toestand

PhD-Thesis, Leiden, 1873
The Netherlands

$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

Two blue arrows point upwards from the text below to the terms nb and a in the equation.

Condensation requires *repulsion* and *attraction*

(lecture 7)

Perfect gas equation of state: no condensation

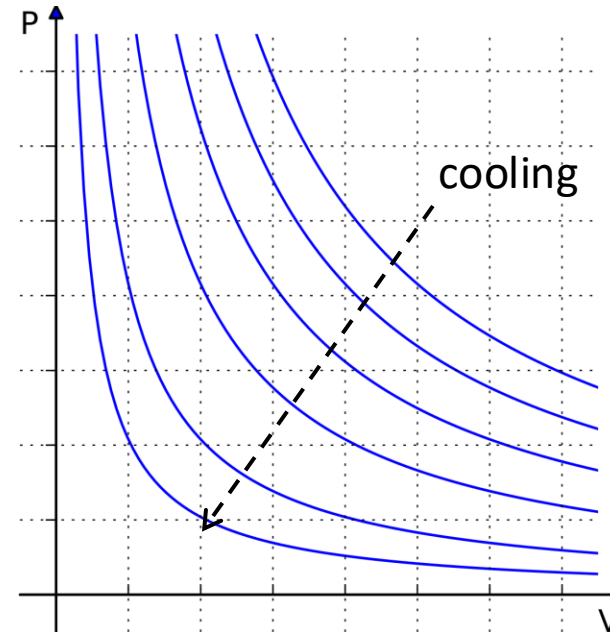
... no interactions ... no condensation ... no matter how far we cool it down ...

Perfect gas isotherms in the P-V plane

$$pV = nRT$$

↓

$$p = \frac{nRT}{V}$$

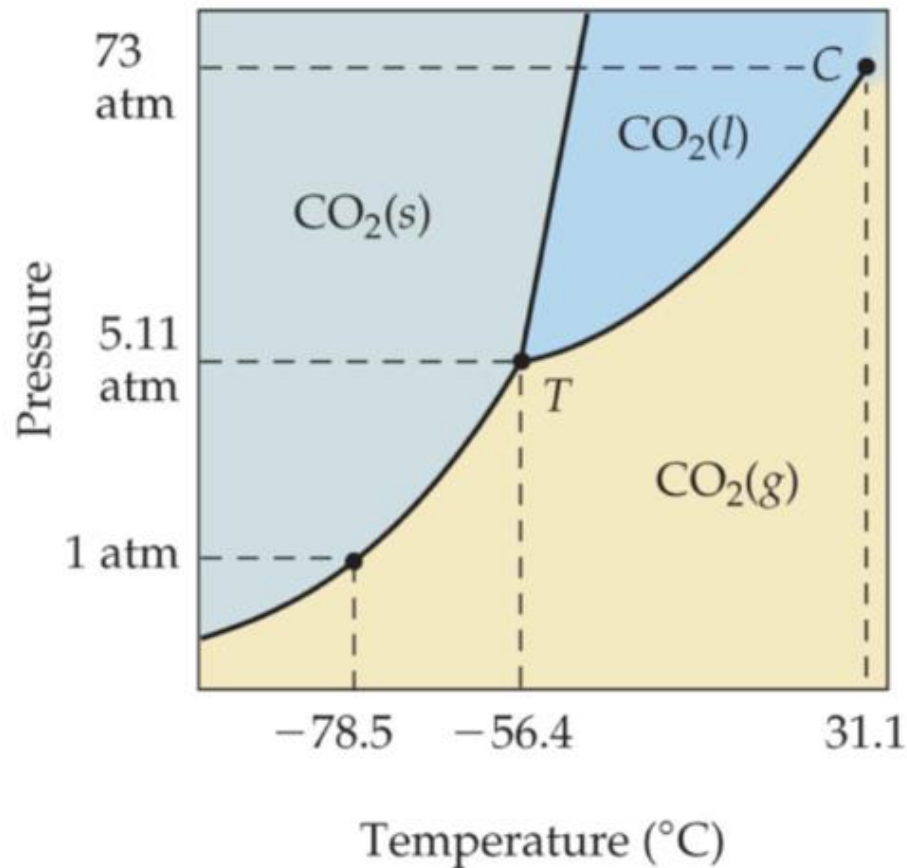


not very realistic ... (as we've seen in Lecture 5: phase diagrams)

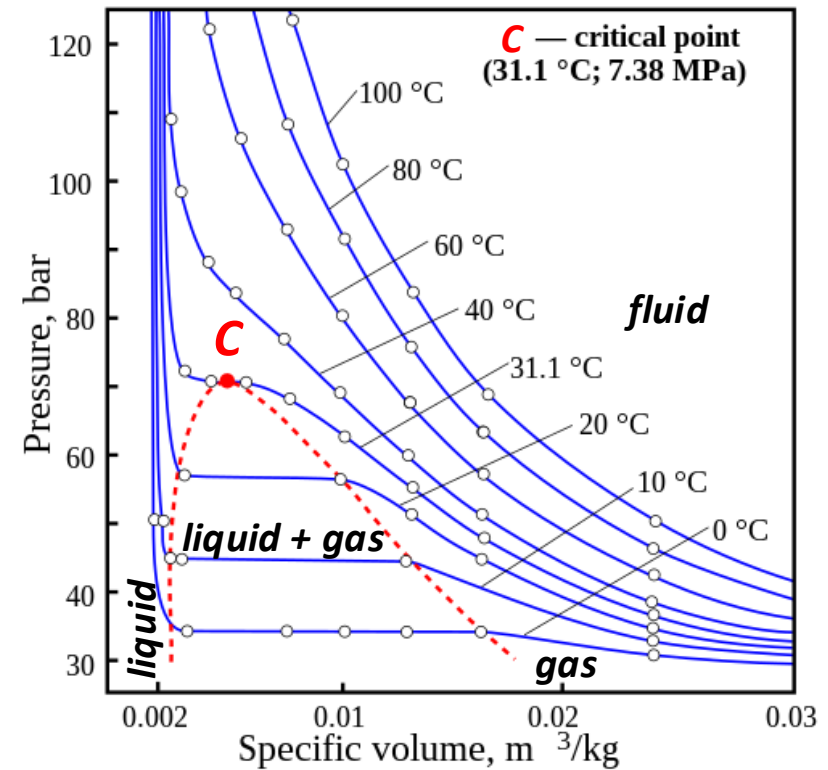
Phase diagram and isotherms of CO₂

Recall from lecture 5:

Phase diagram of CO₂ in the P-T plane



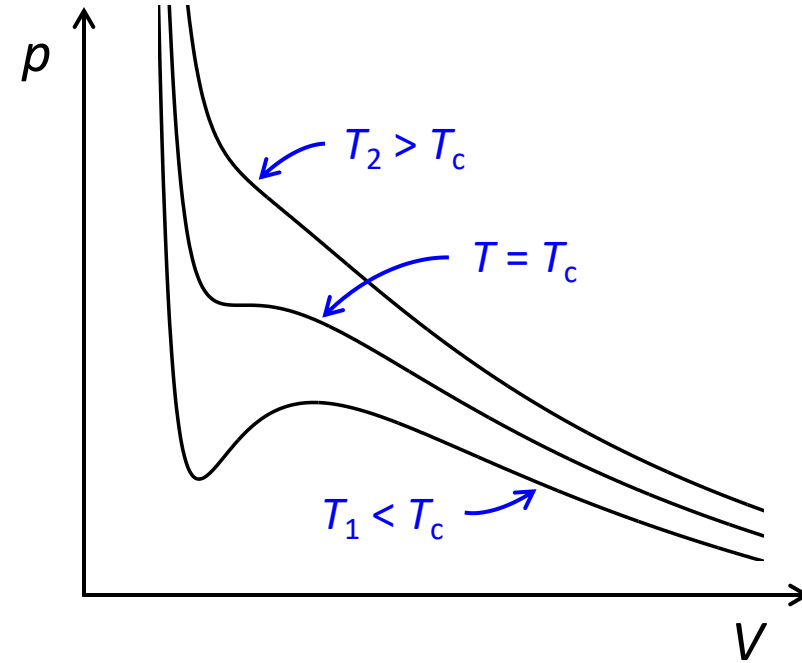
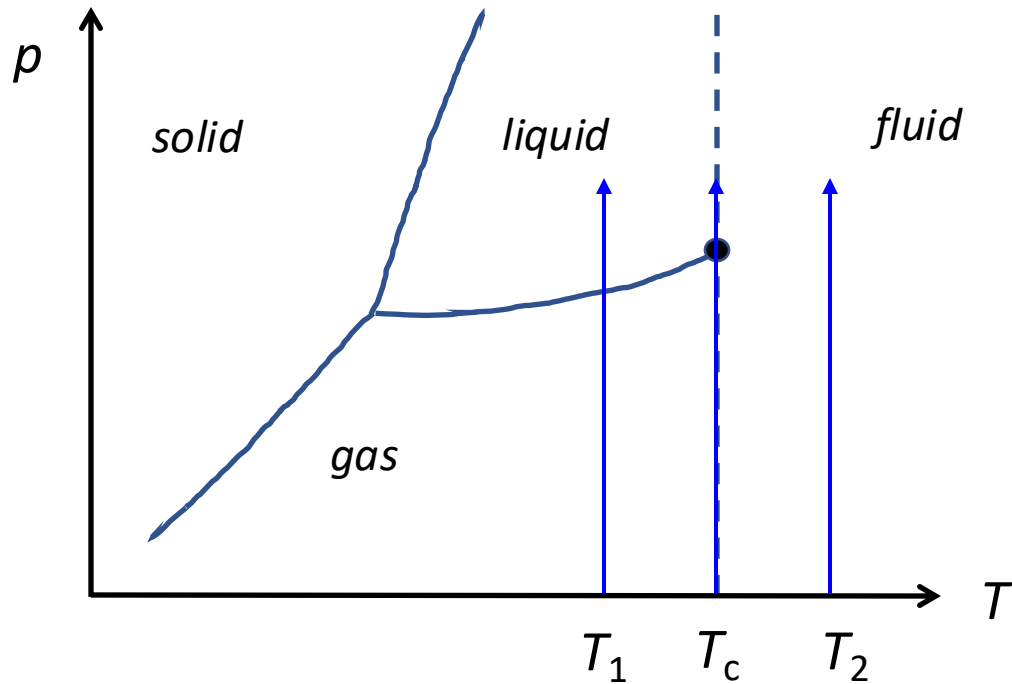
Isotherms of CO₂ in the P-V plane



Isotherms close to the critical point – where condensation happens – are not described by the perfect gas law

Van der Waals isotherms

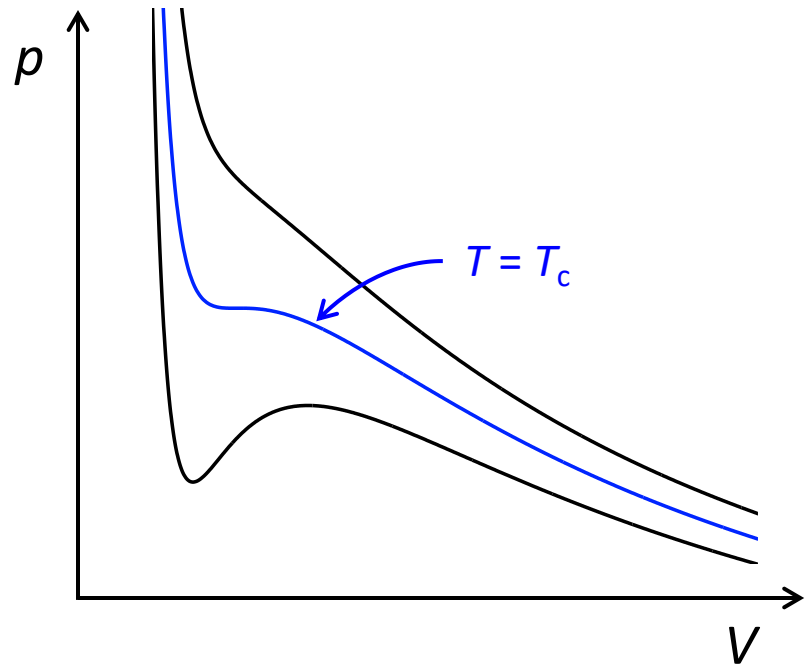
$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$



- $T_2 > T_c$: single fluid phase with perfect gas isotherms at $T_2 \gg T_c$
- $T = T_c$: critical temperature
- $T_1 < T_c$: unphysical 'Van der Waals loops' → liquid-gas coexistence

The critical point for a Van der Waals gas

$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$



At the critical point ($T = T_c, p = p_c, V = V_c$):

$$\left(\frac{\partial p}{\partial V} \right)_T = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0$$

Exercise 35

$$V_{m,c} = 3b$$

$$T_c = \frac{8a}{27Rb}$$

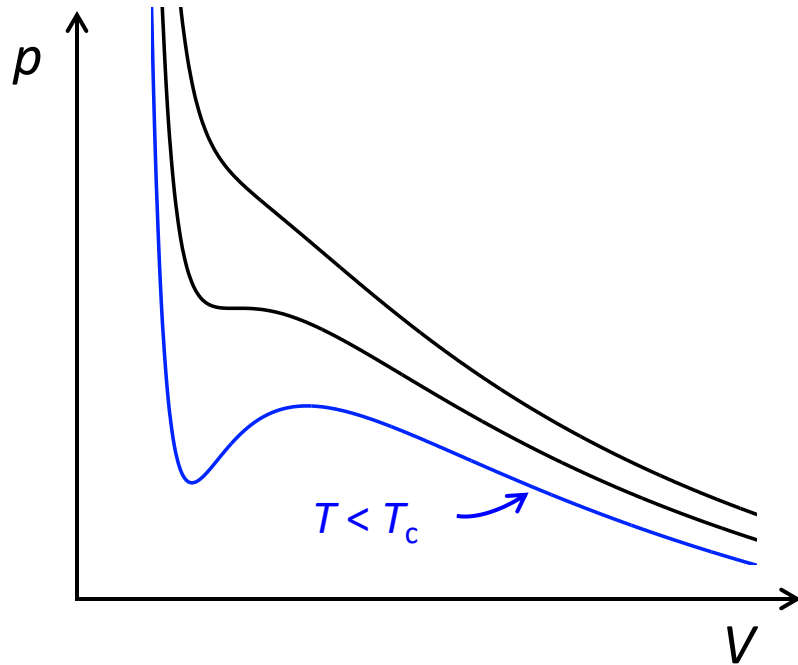
$$p_c = \frac{a}{27b^2}$$

Condensation requires *repulsion* (b) and *attraction* (a)

Van der Waals loops: The Maxwell construction



James Clerk Maxwell
1831 - 1879



and therefore useless, or to present them in a form the details of which could be supplied only by the illegitimate use of the imagination.

J.C. Maxwell, *Nature*, 357, March 4 (1875)

Mr. John Evans, V.P.R.S., president, in the chair.—The Secretary read the reports of the Council and of the Library and Museum Committee. The general position of the Society was described as satisfactory, although, owing to extraordinary expenses during the year, the excess of income over expenditure was but small in comparison with former years. The Society was said to be prosperous, and the number of Fellows to be rapidly increasing.

In presenting the Wollaston Gold Medal to Prof. de Koninck, of Liège, F.M.G.S., the President addressed him as follows:—

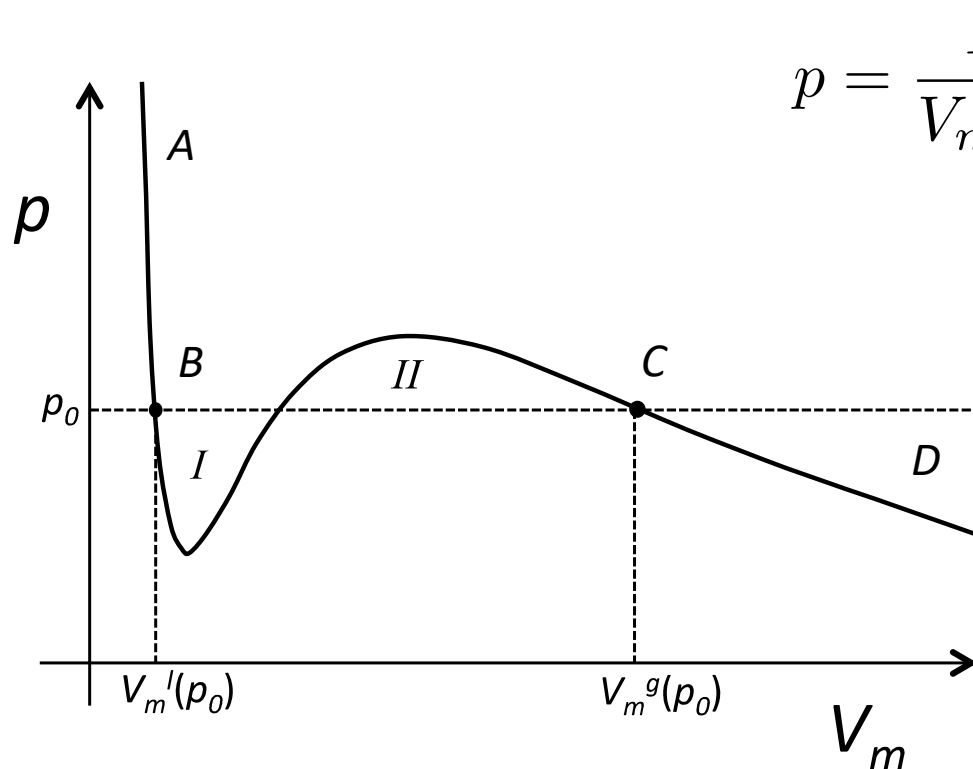
most exactly as the pressure, according to Boyle's Law. As the density continues to increase, the effect of the mutual attraction of the particles becomes sensible, and this causes the rise of pressure to be less than that given by Boyle's Law. If the temperature is low, the effect of attraction may become so large in proportion to the effect of motion that the pressure, instead of always rising as the density increases, may reach a maximum and then begin to diminish. At length, however, as the average distance of the particles is still further diminished, the effect of repulsion will prevail over that of attraction, and the pressure will increase so as not only to be greater than that given by Boyle's Law, but so that a exceedingly small increase of density will produce an enormous increase of pressure.



- Replace unphysical 'Van der Waals loop' by straight line (liquid-gas coexistence)
- Impose condition that this line cuts the loop in equal areas: Area FDE \equiv Area BCD

The Maxwell construction

- Replace unphysical 'Van der Waals loop' by straight line (liquid-gas coexistence)
- Impose condition that this line cuts the loop in equal areas: Area I = Area II



$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Area I = Area II



$\mu_{\text{liquid}} = \mu_{\text{gas}}$ (of course!)

Thanks to Prof Susan Perkin (Oxford)

condensation requires *interactions*

And now for something completely different ...



<https://www.bbc.com/news/av/uk-scotland-63974538>

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- ✓ Chemical Equilibrium and Electrochemistry
- ✓ Ideal solutions, Colligative properties
- ✓ Condensation in the Van der Waals Equation of State

8 Jan 2025, 8:30, HG00.303:

- past exam questions
- Q&A

