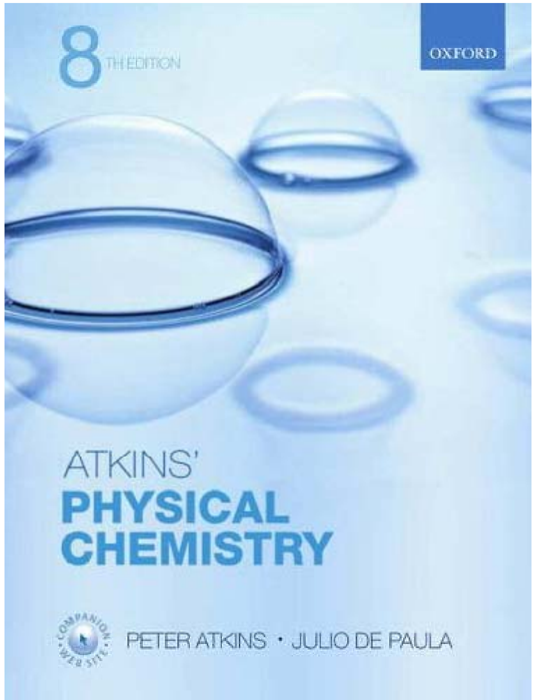
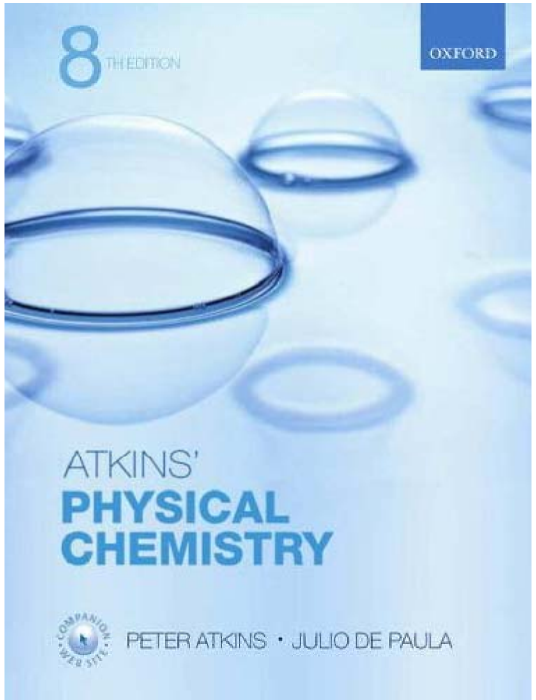
Physical Chemistry

- **Physical chemistry** is the branch of chemistry that establishes and develops the principles of Chemistry in terms of the underlying concepts of Physics



Physical Chemistry



Main book: Atkins' Physical Chemistry 8th edition, Peter Atkins and Julio de Paula

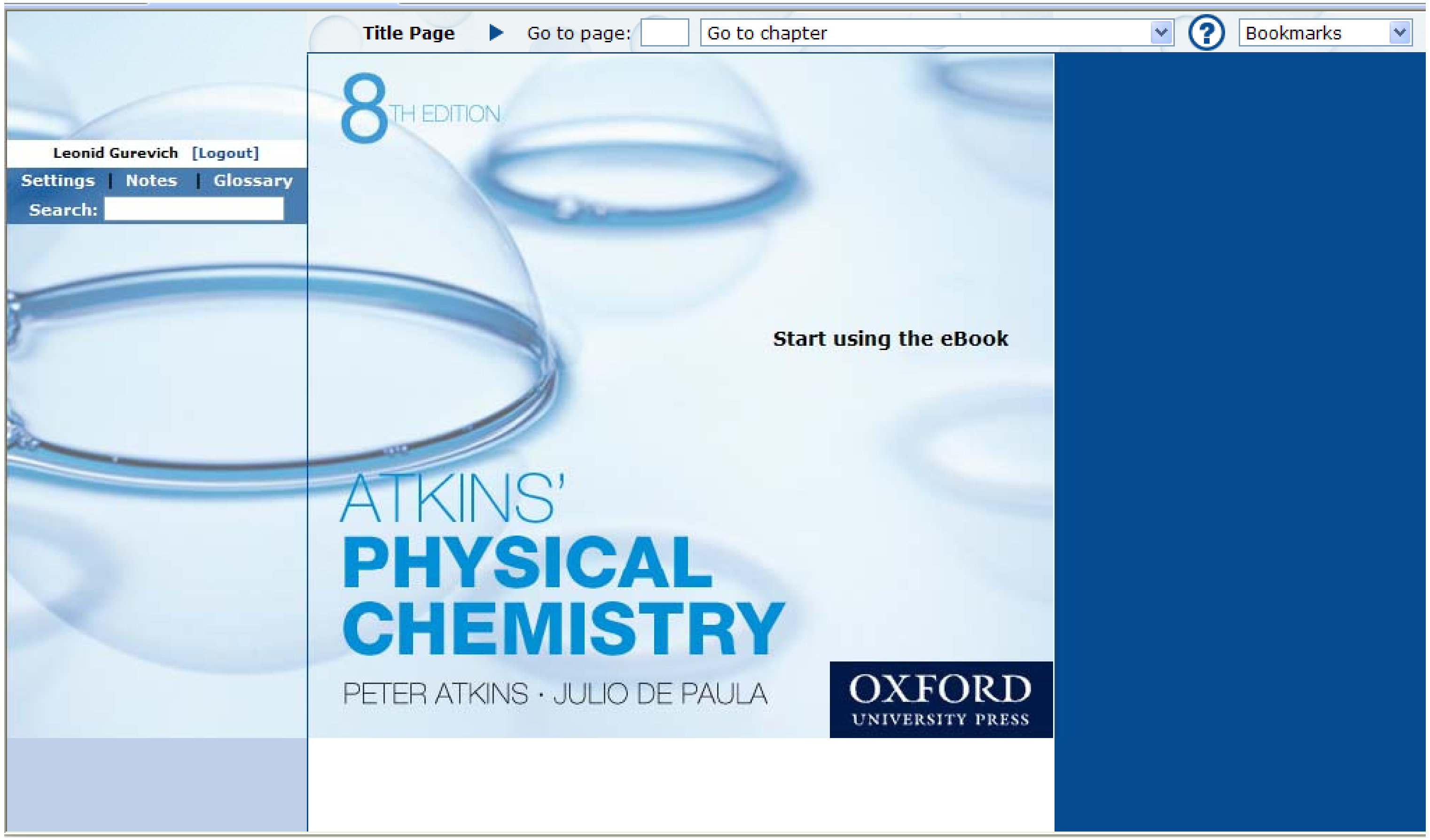
Course web site:
http://homes.nano.aau.dk/lg/PhysChem2009.htm

Schedule

1. Physical transformation of pure substances. Nucleation.
2. Simple mixtures. Activities. Colligative properties.
3. Two components systems and phase diagrams. Phase diagrams in the material science.
4. Chemical Equilibrium. Equilibrium electrochemistry.
5. Molecular motion in gases and liquids.Diffusion and Conductivity.
6. The rates of chemical reactions
7. Kinetics of complex reactions.

Oxford On-Line Resources

- http://www.oup.com/uk/orc/bin/9780198700722/
- e-book:



Leonid Gurevich [Logout]

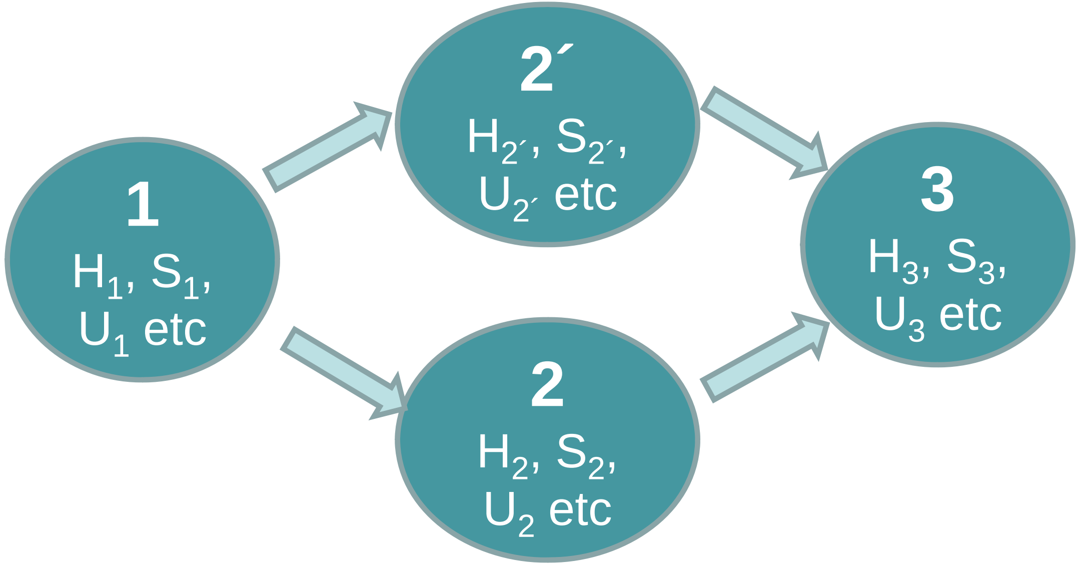
Start using the eBook

Lecture 1

13-10-2008

- Lecture:
  - thermodynamic functions (recap)
  - single component phase diagrams
  - phase transition and phase bondaries
  - surface tension and nucleation
  - new problems

Thermodynamic Functions

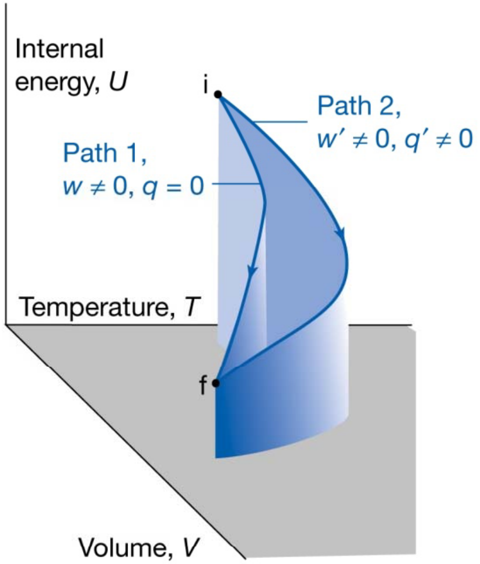


1
H_1, S_1,
U_1 etc

2´
$H_{2'}$, $S_{2'}$,
$U_{2'}$ etc

2
H_2, S_2,
U_2 etc

3
H_3, S_3,
U_3 etc



- State functions: properties that depend on the current state only and on the way it was prepared (e.g. energy and enthalpy)

$$\Delta U = U_f - U_i$$

$$\Delta U = \int_i^f dU$$

Exact differential

- Path functions: relate to the preparation of the state (e.g. work and heat produced)

$$q = \int_{i,path}^{f} dq$$

Enthalpies of transition

- For a chemical reaction, if we define ”standard” conditions for reagents and products the change in the thermodynamic (state) function will not depend on the path or intermediate steps.

- **Hess’s law:** Standard enthalpy (entropy, Gibbs free energy etc.) of an overall reaction is the sum of the enthalpies (entropies, Gibbs free energies etc.) of the individual reaction it may be divided into.

- **Standard state of a substance** at a specified temperature is its pure form at 1 bar

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)\ \Delta H^{\o}=-890kJ/mol$$

$$1mol \qquad 2mol \qquad 1mol \qquad 2mol$$

Unmixed reagents in std.form Unmixed products in std.form

Hess’s Law: Example

Calculate standard reaction enthalpy of combustion of propene if standard reaction enthalpies for combustion of propane and hydrogenetaion of propene into propane are known.

$$CH_2=CHCH_3(g)+H_2 \rightarrow CH_3CH_2CH_3(g) \qquad -124kJ/mol$$

$$CH_3CH_2CH_3(g)+5O_2 \rightarrow 3CO_2(g)+4H_2O(l) \qquad -2220kJ/mol$$

$$H_2O(l) \rightarrow H_2(g)+\frac{1}{2}O_2(g) \qquad +286kJ/mol$$

$$CH_2=CHCH_3(g)+\frac{9}{2}O_2 \rightarrow 3CO_2(g)+3H_2O(l) \qquad -2058kJ/mol$$

Irreversible processes.Clausius inequality

- More energy flows as work under reversible condition: $-dw_{rev} \geq -dw, \quad or \quad dw - dw_{rev} \geq 0$

- On the other hand as internal energy is a state function

$$dU = dw_{rev} + dq_{rev} = dw + dq$$

$$\Rightarrow \; dq_{rev} - dq = dw - dw_{rev} \geq 0 \; \Rightarrow \; dq_{rev} / T \geq dq / T$$

$$\Rightarrow \; \underline{dS \geq dq / T}$$

- In an isolated system the entropy cannot decrease spontaneously $dS \geq 0$

Helmholtz and Gibbs energy

Clausius inequality: $$dS - \frac{dq}{T} \geq 0$$

At constant volume: $$dS - \frac{dU}{T} \geq 0 \qquad TdS - dU \geq 0$$

At constant pressure: $$dS - \frac{dH}{T} \geq 0 \qquad TdS - dH \geq 0$$

Let's define:

- Helmholtz energy $$A = U - TS$$
- Gibbs energy $$G = H - TS$$

Helmholtz and Gibbs energy

- Helmholtz energy:
  - At equilibrium $dA_{T,V} = 0$
    reaction would favorable if $dA_{T,V} < 0$ meaning that total entropy of the system increases (dS entropy change of the system, -dU/T – of the surrounding)
  - The change in Helmholtz energy is equal to the maximum work accompanying the process

Helmholtz and Gibbs energy

- Gibbs energy (free energy):
  - At constant T and P chemical reactions are spontaneous in the direction of decreasing Gibbs energy
  - Maximum additional (non-expansion) work is given by the change in Gibbs energy.
  - Standard Gibbs energy can be defined as:

$$\Delta_r G^{\theta} = \Delta_r H^{\theta} - T\Delta_r S^{\theta}$$

Further, standard Gibbs energy of formation can be introduced:

$$\Delta_f G^{\theta} = \sum_{\text{Products}} \nu\Delta_f G^{\theta} - \sum_{\text{Reactants}} \nu\Delta_f G^{\theta}$$

Combining the First and Second Law

$$dU = \underset{\swarrow}{dq} + \underset{\searrow}{dw}$$

$$\boxed{TdS} \qquad \boxed{-pdV}$$

For closed system in the absence of additional work

$$\underline{dU = TdS - pdV}$$

Fundamental equation

Can be applied to reversible and irreversible changes

Mathematically:

So,

$$dU = \underset{\swarrow}{\left(\frac{\partial U}{\partial S}\right)_V} dS + \underset{\searrow}{\left(\frac{\partial U}{\partial V}\right)_S} dV$$

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_V = T} \qquad \boxed{\left(\frac{\partial U}{\partial V}\right)_S = -p}$$

Properties of Gibbs energy

$$G = H - TS$$

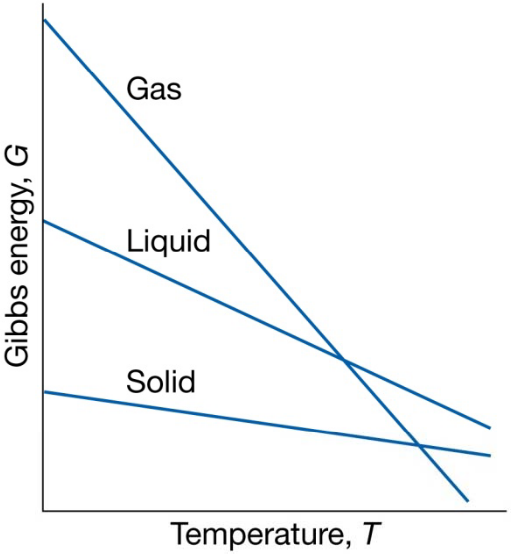
$$dG = -SdT + Vdp$$

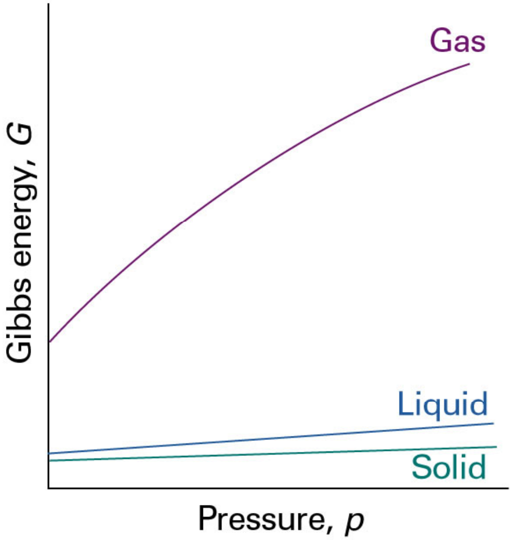
$$\boxed{\left(\frac{\partial G}{\partial T}\right)_p = -S} \qquad \boxed{\left(\frac{\partial G}{\partial p}\right)_V = V}$$

- G decreases with temperature, proportional to entropy

Gibbs-Helmholtz equation

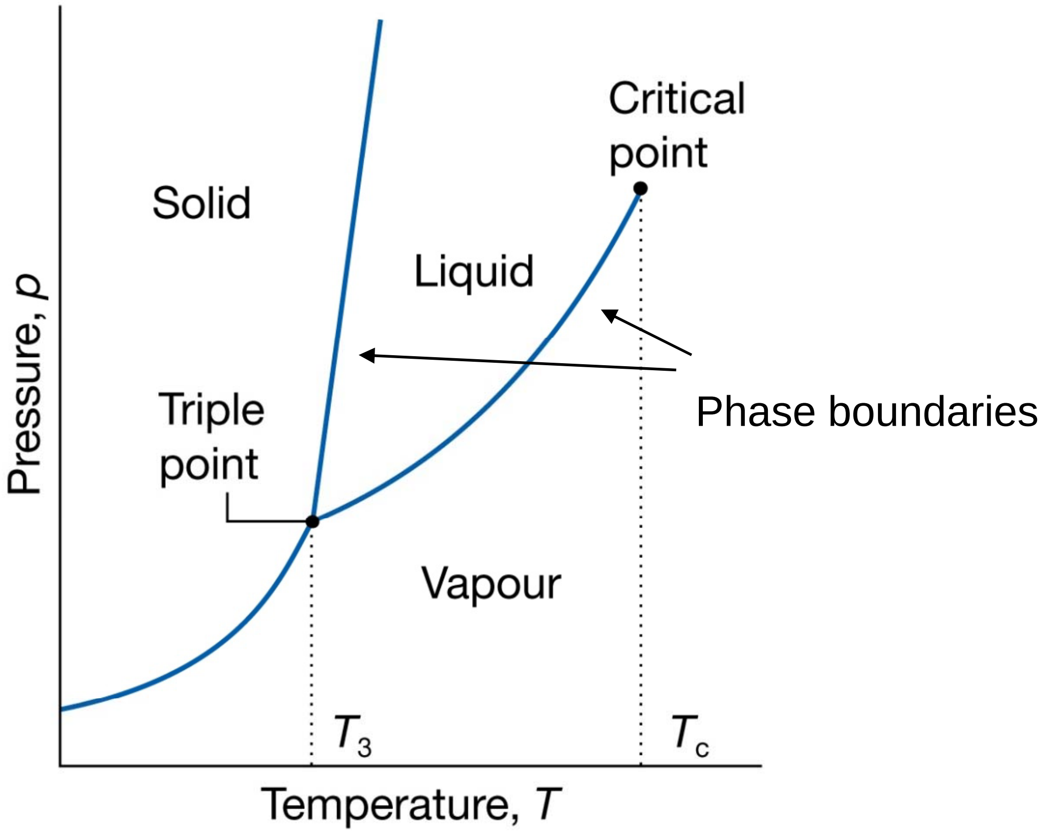
$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \Rightarrow \left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = -\frac{H}{T^2}$$



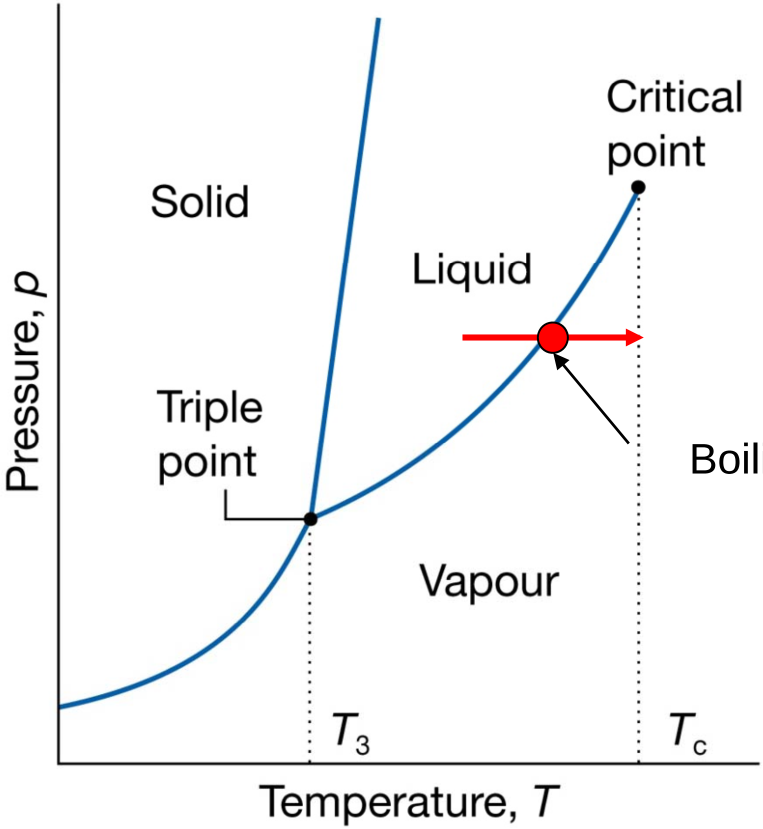


Phase diagrams

- **Phase** – a form of matter that is uniform through in chemical composition and physical state
- **Phase transition** – a spontaneous conversion of one phase into another
- **Transition temperature** – a temperature at which two phases are in equilibrium
- **Metastable phase** – thermodynamically unstable phase that persist because the transition is kinetically hindered



Phase boundaries

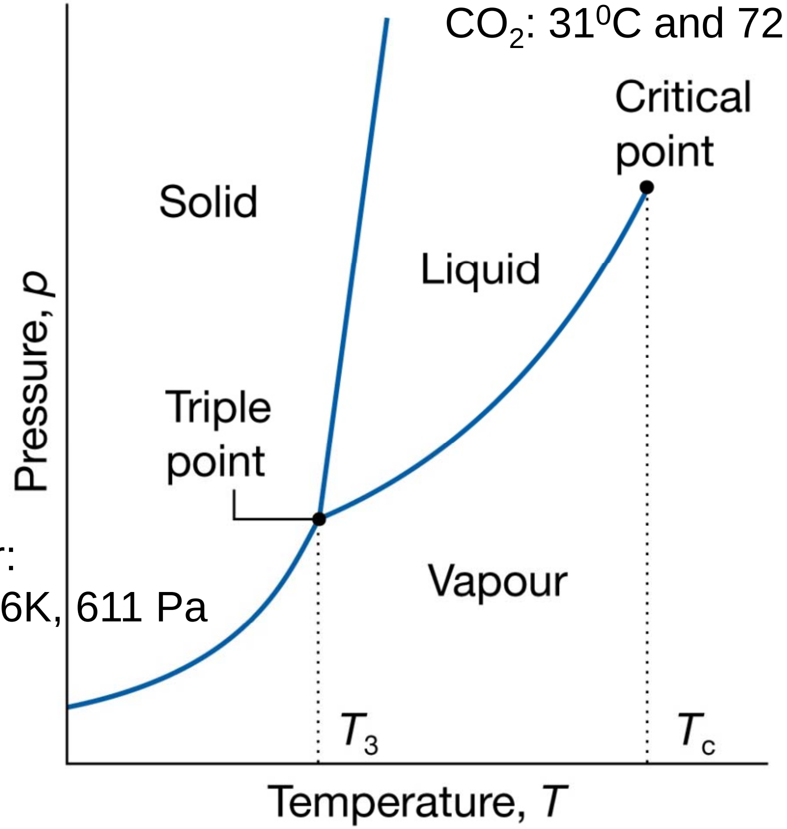


Boiling point

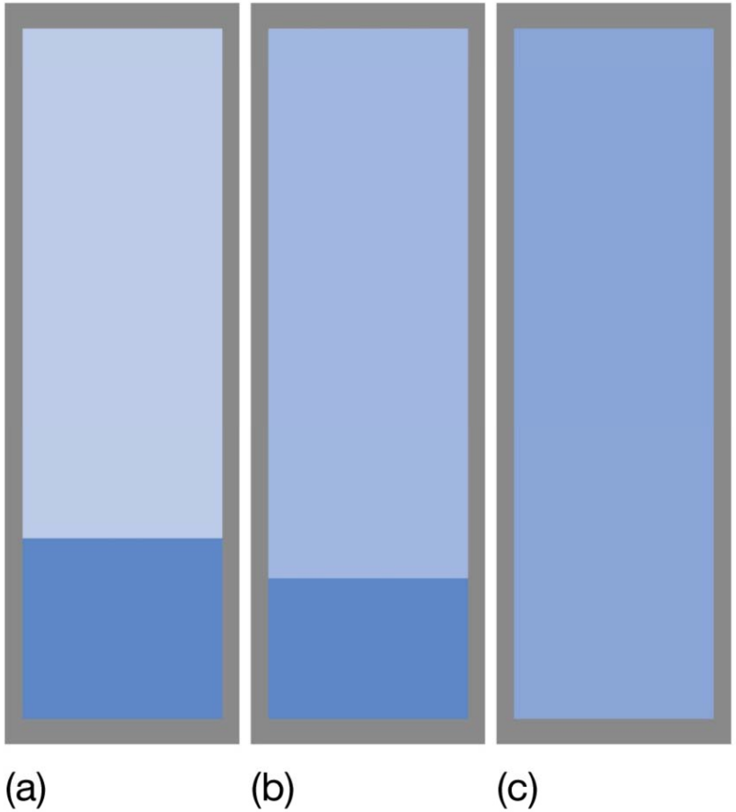
Boiling temperature – the temperature at which vapour pressure is equal to external pressure

Phase boundaries

Supercritical liquid
water: 374^{0}C and 218 atm
CO_2: 31^{0}C and 72.9 atm



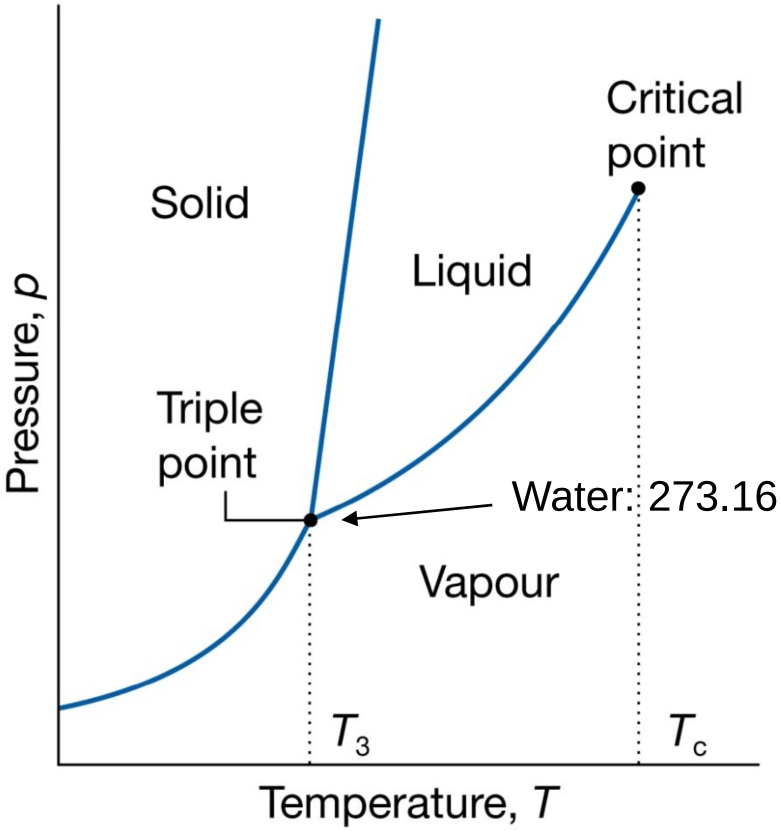
Water:
273.16K, 611 Pa



Heating liquid in a closed vessel

Applications: Supercritical drying; dry cleaning; supercritical fluid chromatography

Phase boundaries

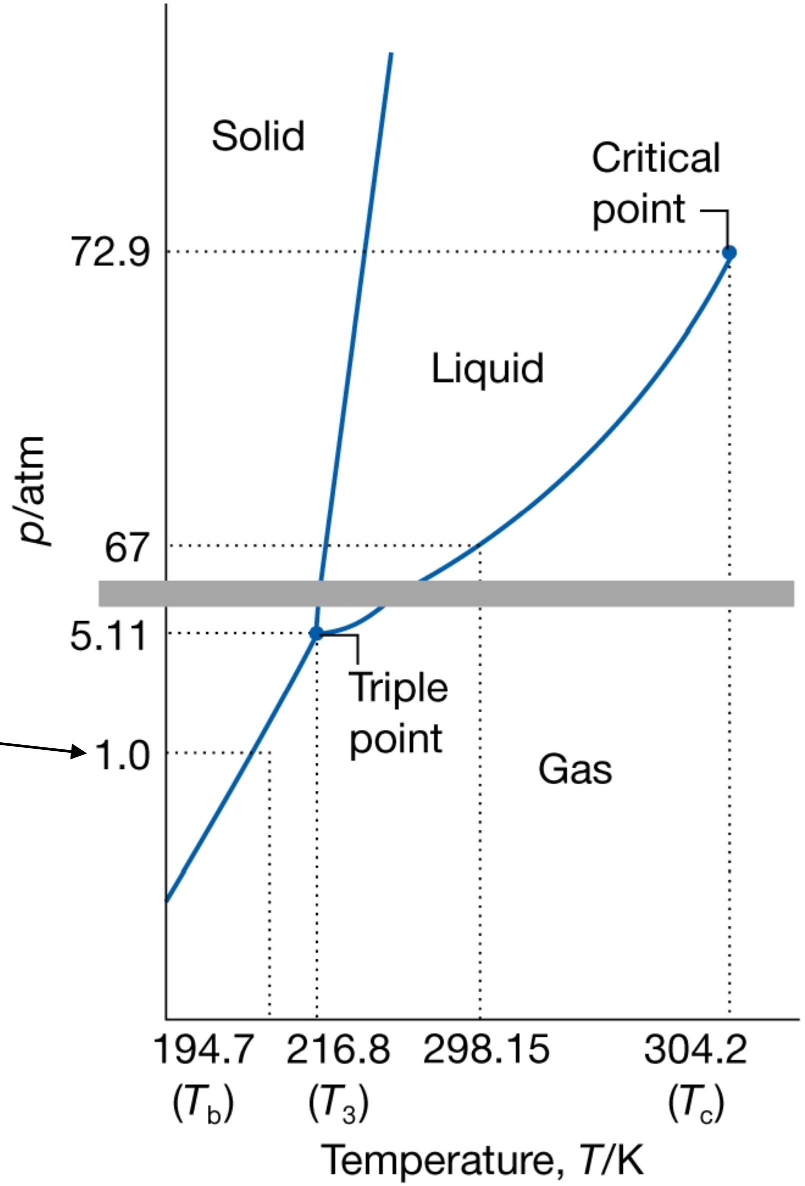


Water: 273.16K and 611 Pa

Melting (freezing) temperature – the temperature at which liquid and solid phases coexist in equilibrium (at given pressure). Melting temperature at 1 atm called **normal**, at 1bar – **standard**

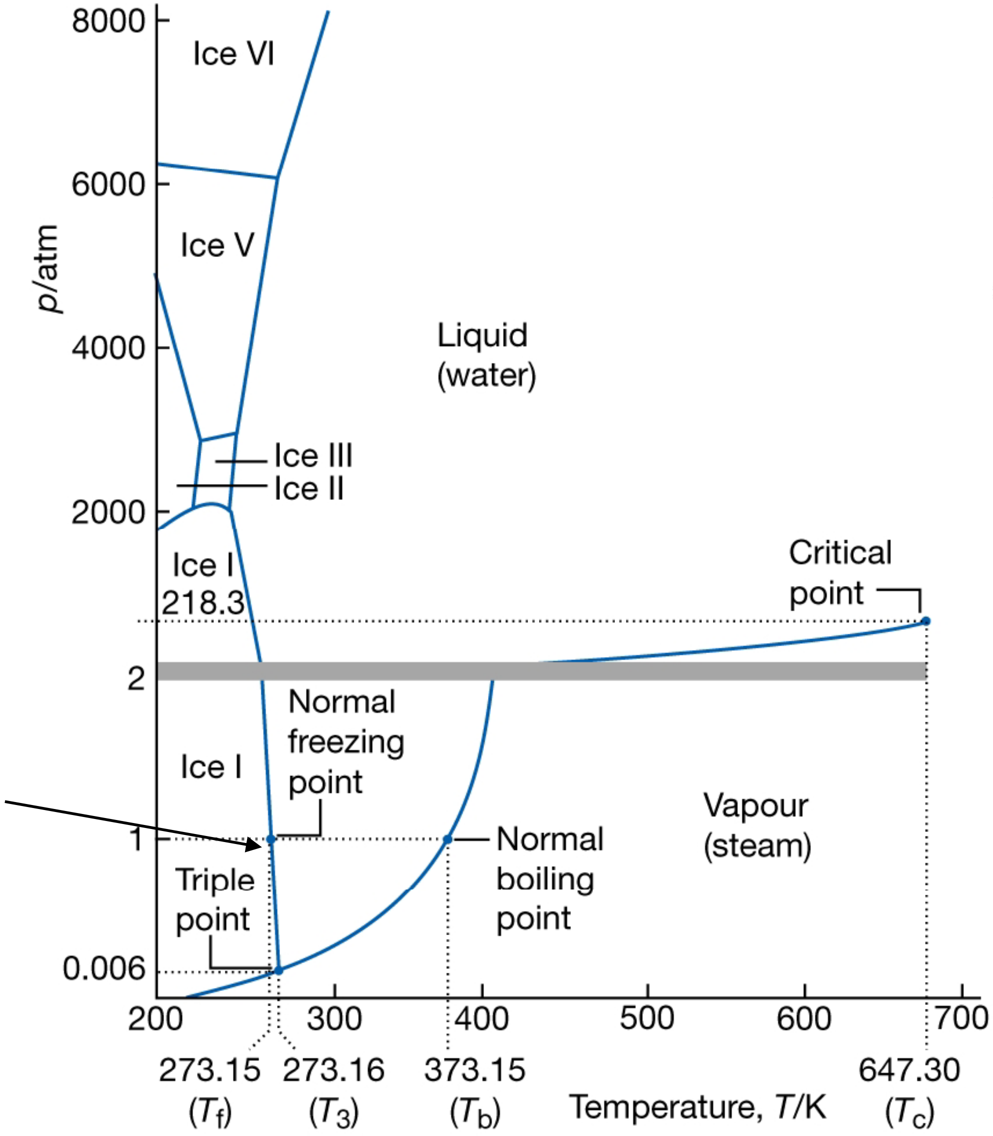
Triple point (T_3) - the point at which the three phases coexist.

Phase diagrams: CO_2

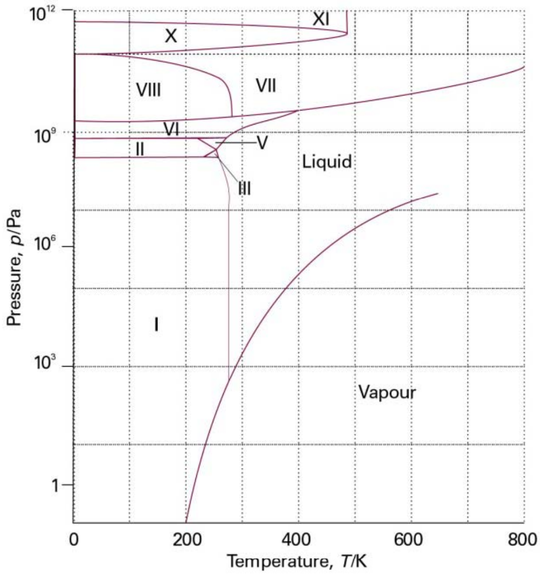


At atmospheric pressure “dry-ice” forms directly form gas

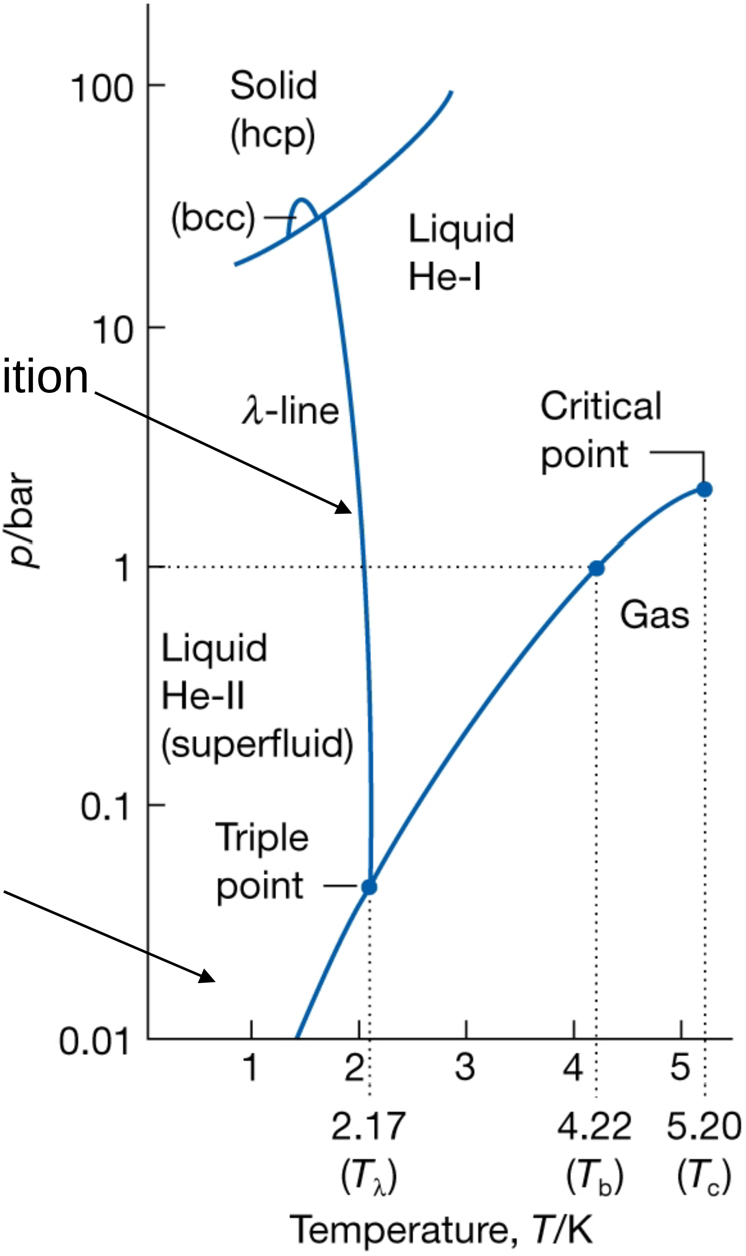
Phase diagrams: water



Negative slope



Phase diagrams: ^{4}He



Liquid-liquid transition

Stays liquid at 0K

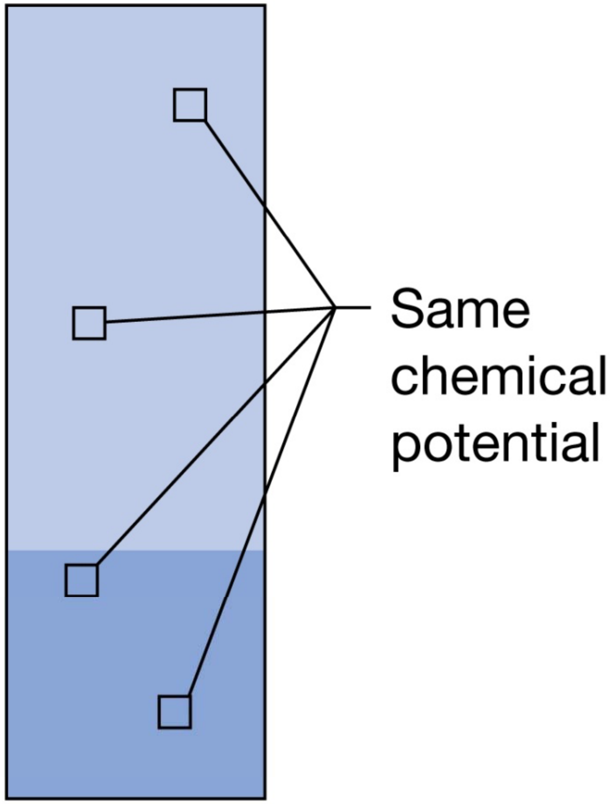
Phase transitions

- Chemical potential $\mu = G_m$ for a one-component system
- At equilibrium chemical potential is the same through the system

Otherwise, if chemical potential is different, we can find a place with higher chemical potential μ_1 and exchange material from there with another place at chemical potential μ_2.

$$dG = \mu_2 dn - \mu_1 dn = (\mu_2 - \mu_1) dn < 0$$

Spontaneous process could take place, so the system is out of equilibrium



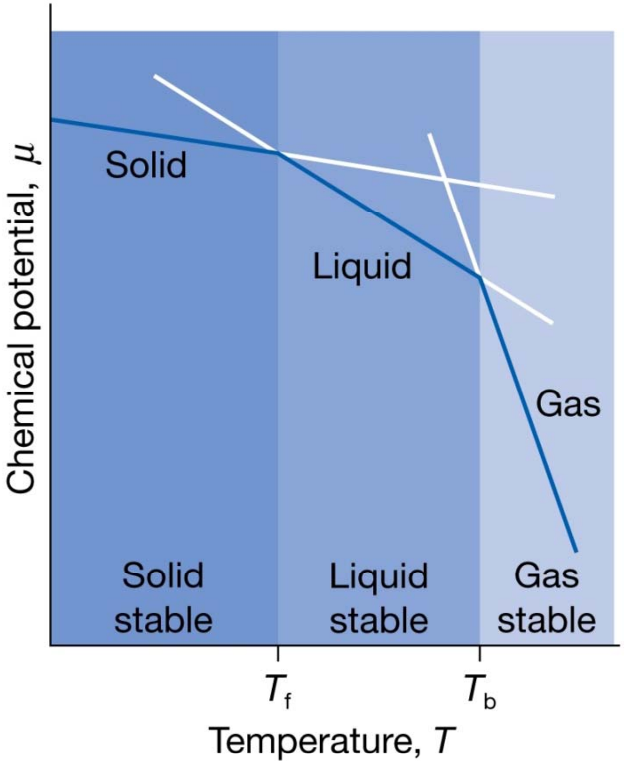
Phase transitions $dG = -SdT + Vdp,\ \mu = G_m$

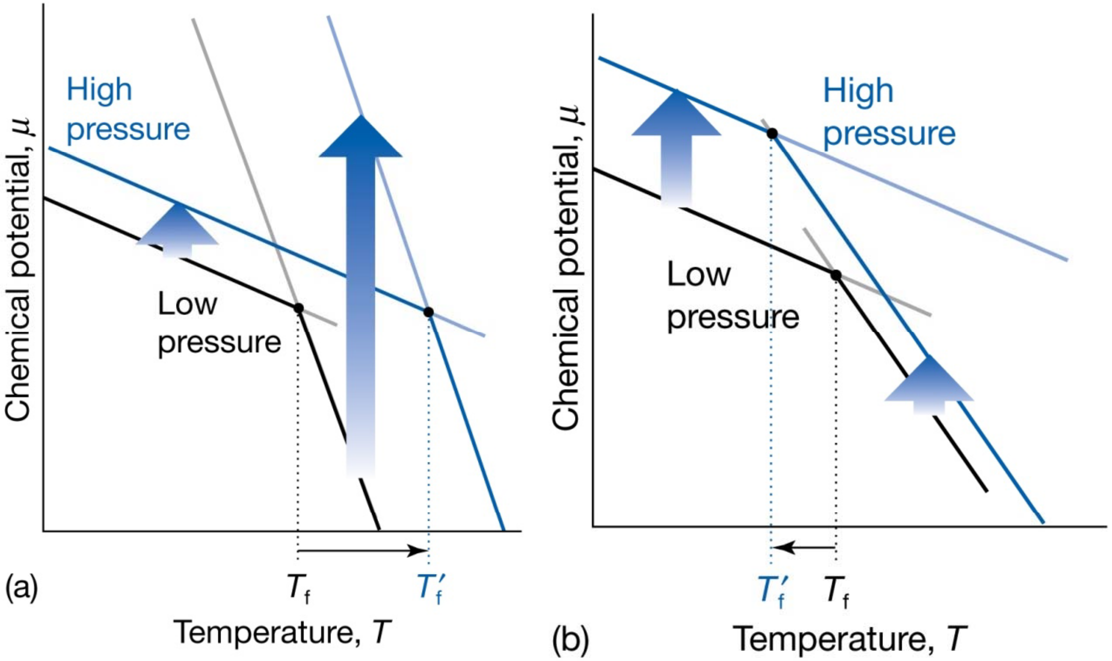
Temperature dependence

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

Melting point vs. applied pressure

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





Phase transitions

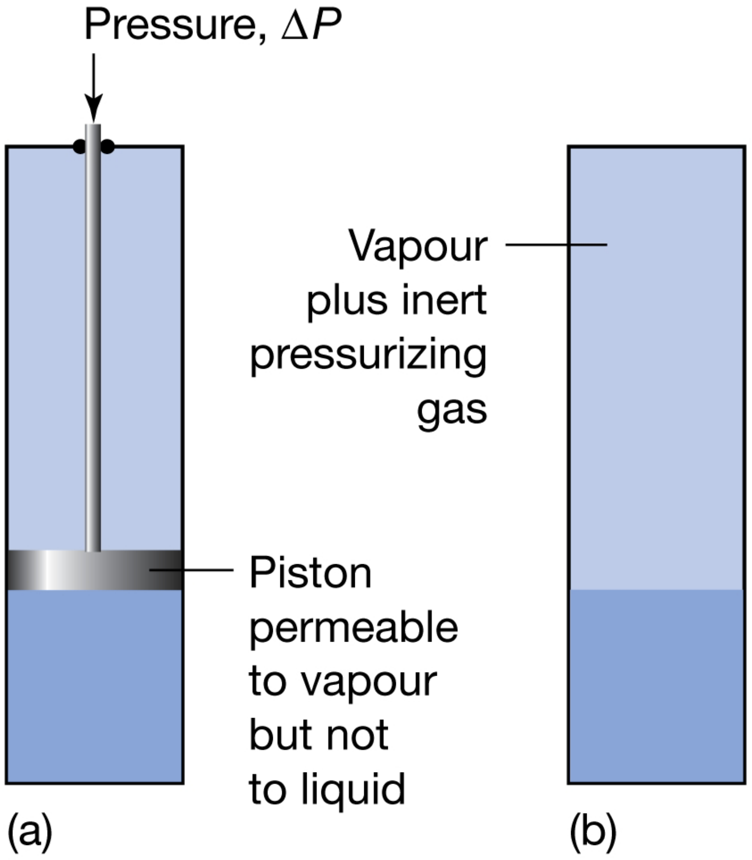
The effect of applied pressure on vapour pressure

- when pressure applied to a condensed phase its vapour pressure rises: molecules squeezed and escape as a gas.

$$p = p^{*}\exp(V_m\Delta P / RT)$$

New vapour pressure

vapour pressure
in the absense of add.pressure



Indeed:

$$d\mu(\text{gas}) = d\mu(\text{liq})$$

$$RTdp / p = V_m(\text{liq})dP$$

$$RT\int_{p^{*}}^{p}\frac{dp}{p} = \int_{p^{*}}^{p^{*}+\Delta P} V_m dp$$

$$RT\ln\left(\frac{p}{p^{*}}\right) = V_m\Delta P$$

$$p = p^{*}\exp(V_m\Delta P / RT) \Longrightarrow p = p^{*}(1+V_m\Delta P / RT)$$

Location of phase boundaries

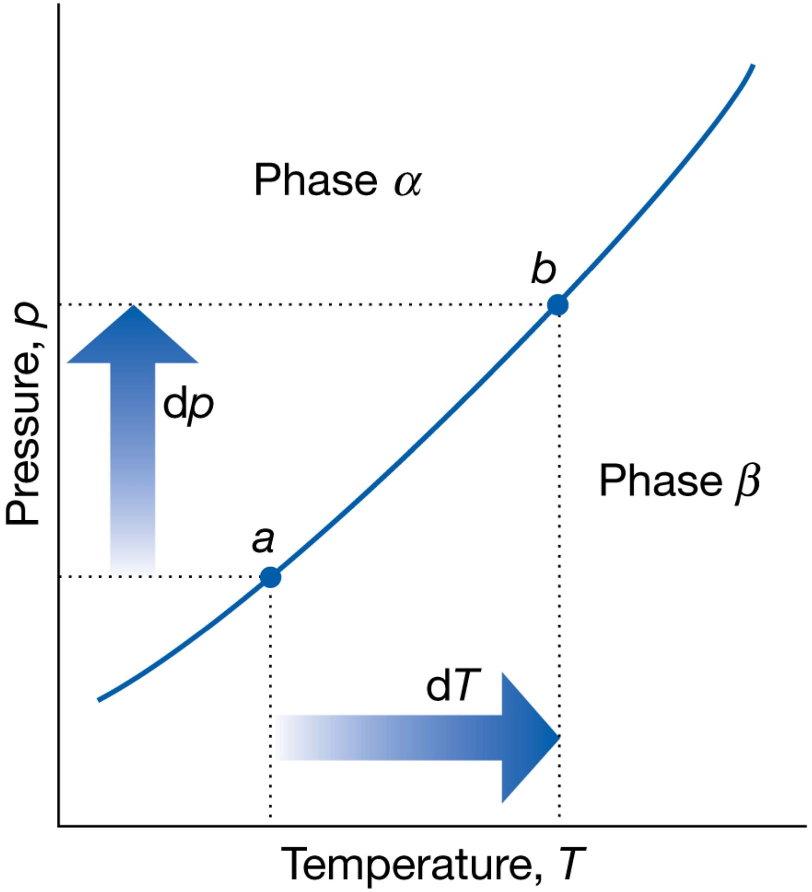
$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

$$d\mu = -S_m dT + V_m dp$$

$$-S_{\alpha,m} dT + V_{\alpha,m} dp = -S_{\beta,m} dT + V_{\beta,m} dp$$

Clapeyron equation:

$$\frac{dp}{dT} = \frac{S_{\alpha,m} - S_{\beta,m}}{V_{\alpha,m} - V_{\beta,m}}$$



- Exact equation that applies to any phase transition of pure substance

Location of phase boundaries

Solid-liquid boundary

usually>0

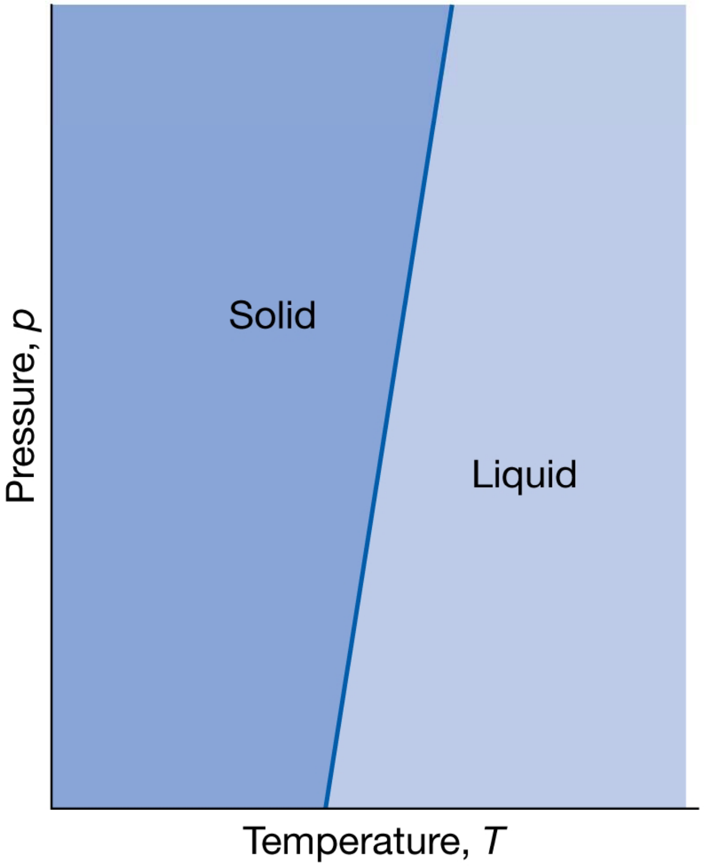
$$\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}$$

usually>0 and small

$$\int_{p^*}^{p} dp = \frac{\Delta_{fus} H}{\Delta_{fus} V} \int_{T^*}^{T} \frac{dT}{T}$$

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

$$p \approx p^* + \frac{\Delta_{fus} H}{T^* \Delta_{fus} V}\left(T - T^*\right) \qquad when \frac{T - T^*}{T^*} \ll 1$$



Location of phase boundaries

Liquid-vapour boundary

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

usually>0 and large

usually>0 and large

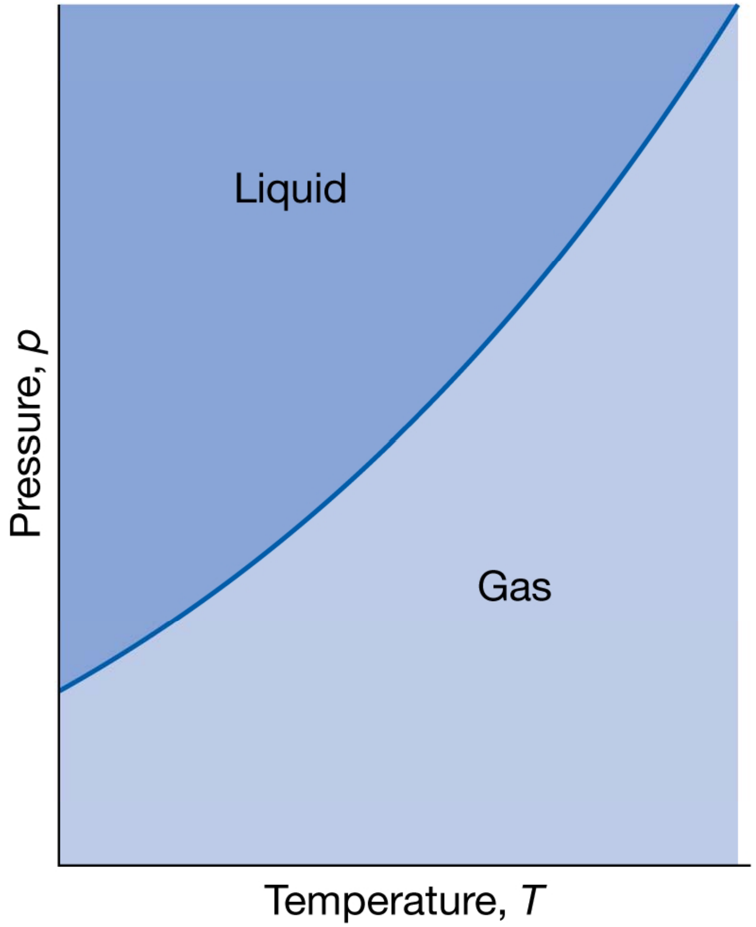
If we assume perfect gas and $V_m(\text{liq}) \ll V_m(\text{gas})$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)}$$

Clausius-Clapeyron equation

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

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

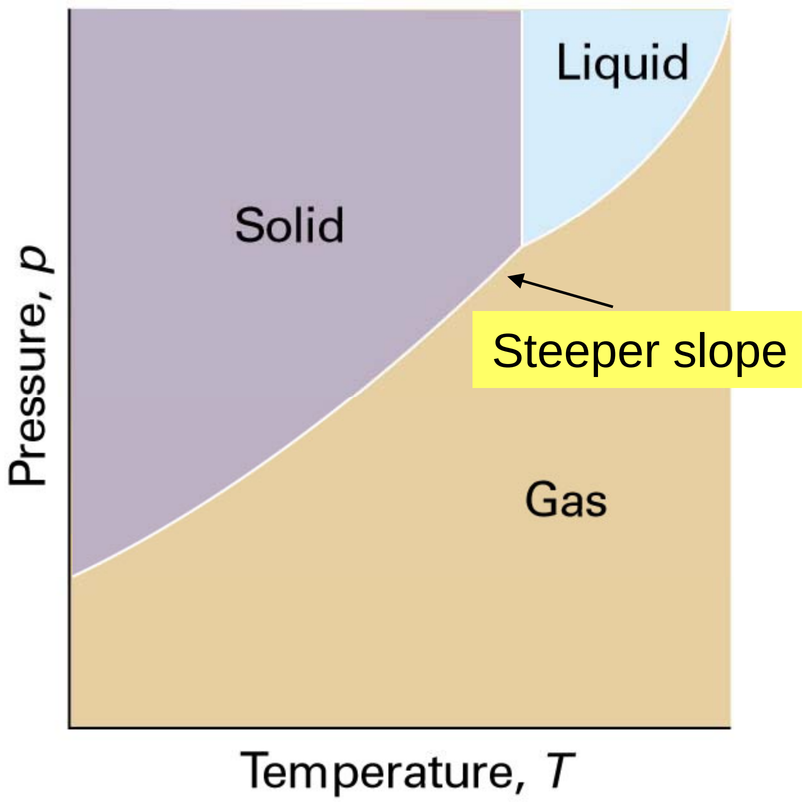


Location of phase boundaries

solid-vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{sub}H}{T\Delta_{sub}V} = \frac{\Delta_{fus}H + \Delta_{vap}H}{T\Delta_{sub}V}$$

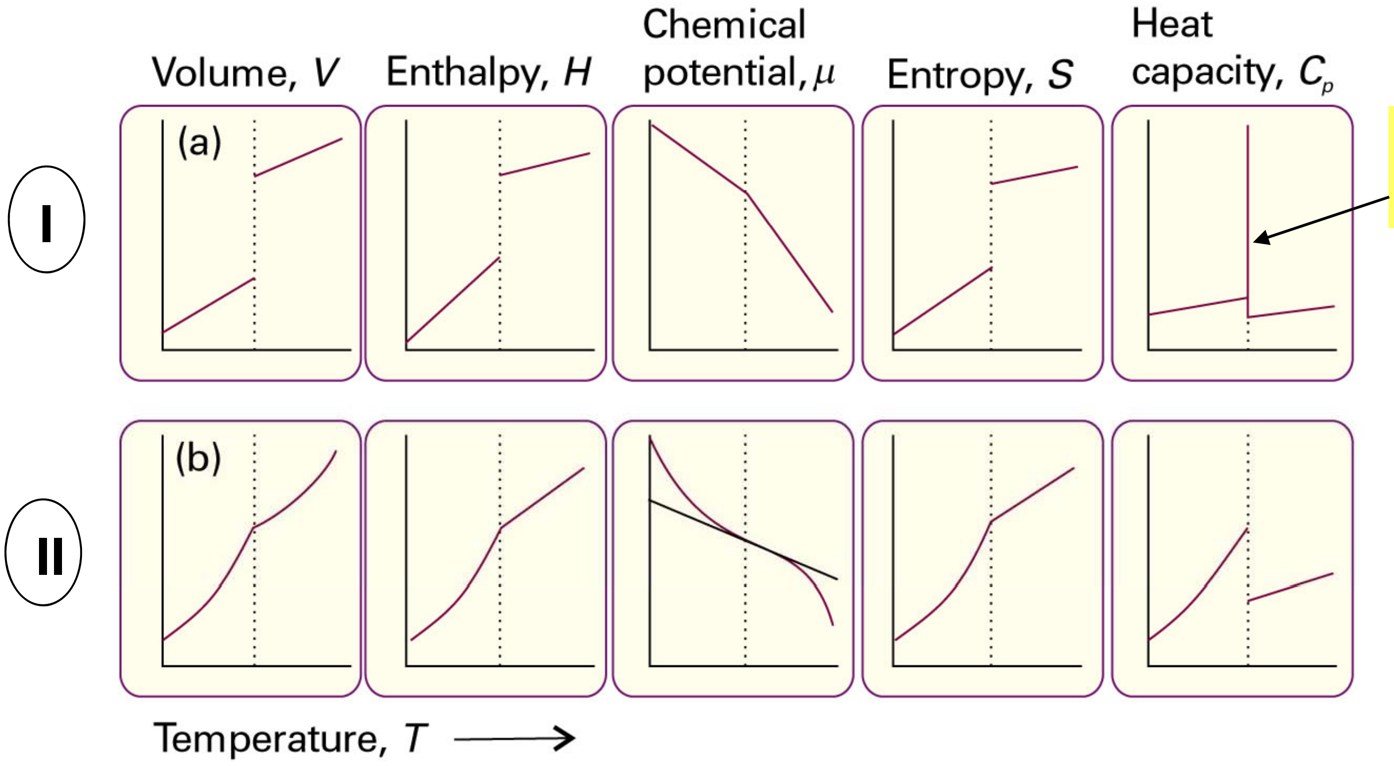
$$\approx \Delta V_{vap}$$



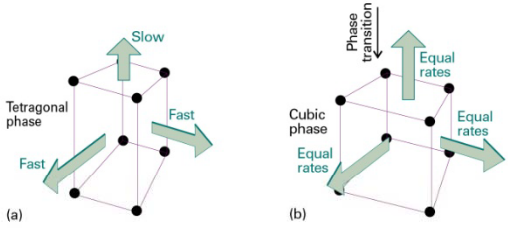
Ehrenfest classification of phase transitions

$$\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{trs} V, \qquad \left(\frac{\partial \mu_\beta}{\partial T}\right)_p - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_p = -S_{\beta,m} + S_{\alpha,m} = \Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

- **First order transition**: **first derivatives** of the chemical potential with respect to temperature and pressure **are discontinuous**.
- **Second order** phase transition: first derivative of the chemical potential is continuous but the **second derivative is discontinuous**. Though the symmetry changes abruptly at the point of transition, the state of the phase changes continuously
- **Lambda-transition** – first derivative continuous but heat capacity is infinite at T_{trs}.



Infinite at transition

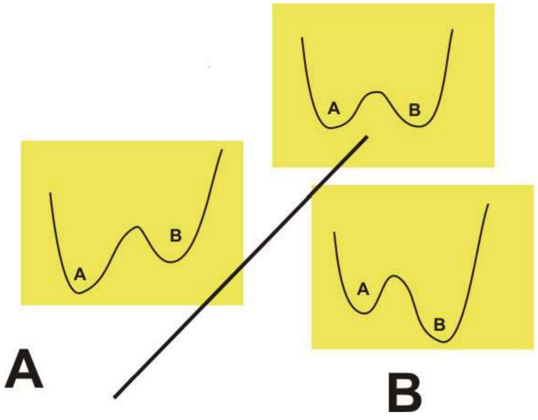


Phase Transitions

First Order	**Second Order**
Melting; Vaporization; most of solid state transitions (like “tin pest” b (white) ->a (grey))	Ferromagnetism (H=0); Superconductivity; Superfluidic Liquid crystals

- Phase transition = change in symmetry

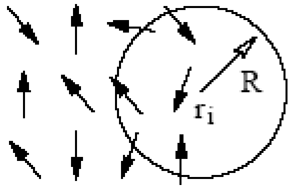
Abrupt change, two states coexist



Overcooling/overheating is possible

Smooth transition

Example: XY-ferromagnet



Order parameter: local magnetization

$$\mathbf{m}(\mathbf{r}_i) = \frac{1}{R^d} \sum_{|\mathbf{r}_j - \mathbf{r}_i| < R} \mathbf{S}_j$$

Surface Tension

- Physical boundary between phases can posses extra energy, therefore work is required do change the area:

$$dw = \gamma d\sigma$$

Surface tension

- Minimization of surface energy often results in formation of a bubble or cavity. Let’s consider force balance in a spherical cavity:

$$d\sigma = 4\pi(r+dr)^2 - 4\pi r^2 = 8\pi r dr \quad \Rightarrow \quad dw = 8\pi\gamma r dr \quad \Rightarrow \quad F = 8\pi\gamma r$$

$$F = 4\pi r^2 p$$

$$4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi\gamma r$$

$$p_{in} = p_{out} + 2\gamma / r$$

Vapour pressure of a droplet (from Kelvin equation) $p = p^* \exp(2\gamma V_m / rRT)$

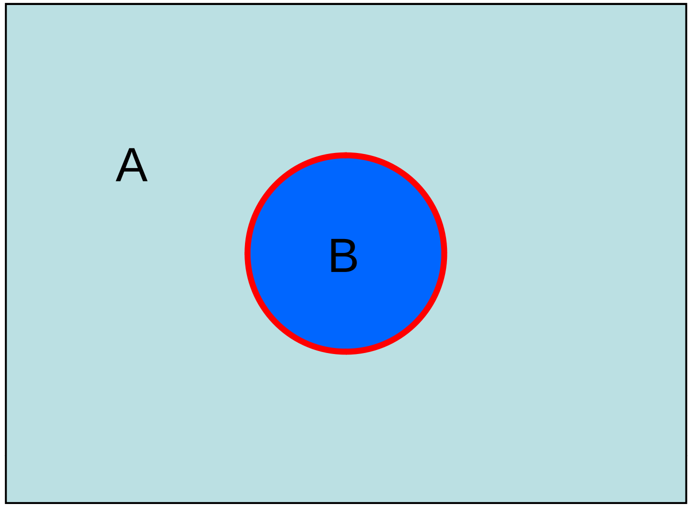
For water: $p(r = 0.1\mu m) = 1.011 p^*$ $p(r = 1nm) = 2.95 p^*$

Surface tension

- **Nucleation**

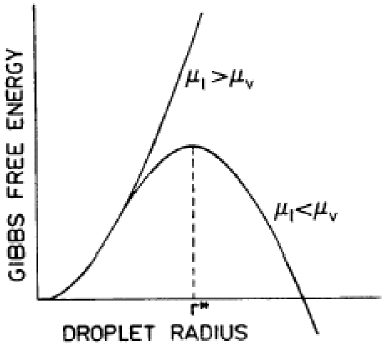
Seed of the new phase will grow only if Gibbs free energy of the system decreases

Significant surface energy has to be created to separate phases at the onset of phase transition



$$\Delta G = -\frac{4\pi r^3}{3V_m}\Delta\mu + 4\pi r^2\gamma$$

$$\frac{\partial}{\partial r}\Delta G = -\frac{4\pi r^2}{V_m}\Delta\mu + 8\pi r\gamma \qquad r^* = \frac{2\gamma V_m}{\Delta\mu}$$



As a result at the phase transition only the nucleation center with **infinite** radius will grow. All finite nucleation center require finite **thermodynamic force**: $\Delta\mu > 0$

Problems

To solve in class:

- **4.7a**: An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 5.0 m × 5.0 m × 3.0 m at 25°C. What mass of each substance will be found in the air if there is no ventilation? (The vapour pressures are (a) 3.2 kPa, (b) 13.1 kPa, (c) 0.23 Pa.)
- **4.9a** Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.
- **4.10a** What fraction of the enthalpy of vaporization of water is spent on expanding water vapour

To solve at home:

- **P4.5:** Calculate the difference in slope of the chemical potential against pressure for water on either side of (a) normal freezing point (b) normal boiling point. The densities of ice and water at 0ºC are 0.917 g cm^{-3} and 1.0 g cm^{-3} and those of water and water vapour at 100ºC are 0.958 g cm^{-3} and 0.598 g cm^{-3}, respectively. By how much the chemical potential of water vapour exceed that of liquid water at 1.2 atm and 100ºC.
- **P4.7**: 50 dm3 of dry air is slowly bubbled through a thermally insulated beaker containing 250g of water initially at 25ºC. Calculate the final temperature assuming the vapour pressure of water constant at 3.17kPa, its heat capacity 75.5 JK-1mol-1 and it behaves as a perfect gas. Assume that the temperature of air is constant.

If you need any extra data to solve the problems, search for them in the Data section in the end of the Atkins book!