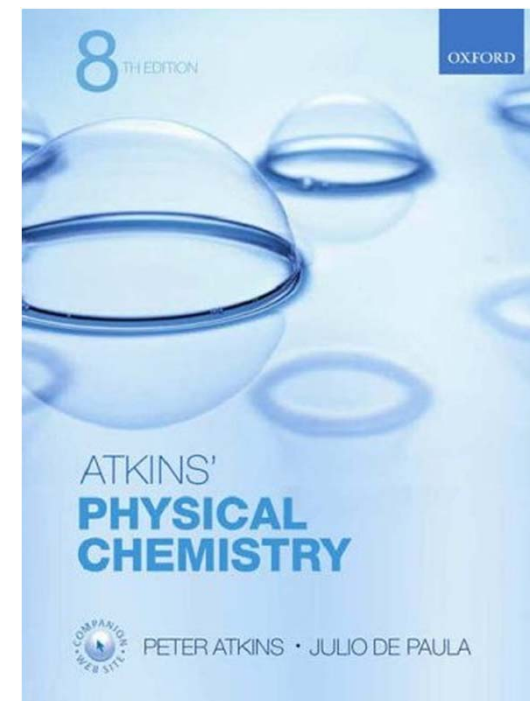# Physical Chemistry

- **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

<u>Main book:</u> Atkins' Physical Chemistry 9th ed.,
Peter Atkins and Julio de Paula

Course web site:
**http://homes.nano.aau.dk/lg/PhysChem2010.htm**

<u>Schedule</u>

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.
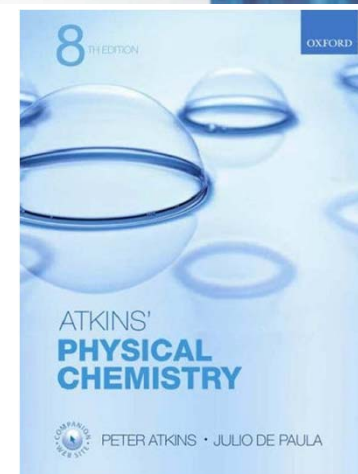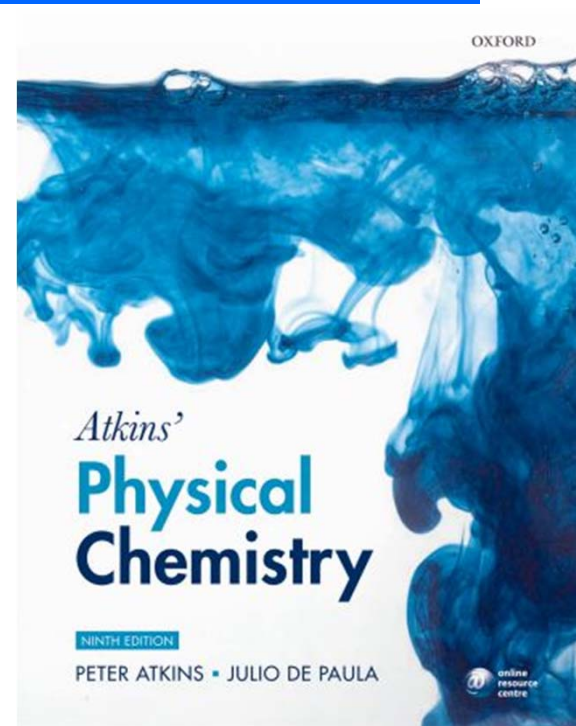
# Oxford On-Line Resources

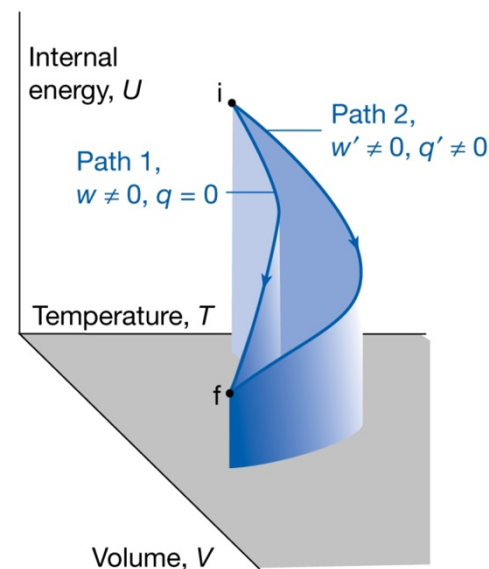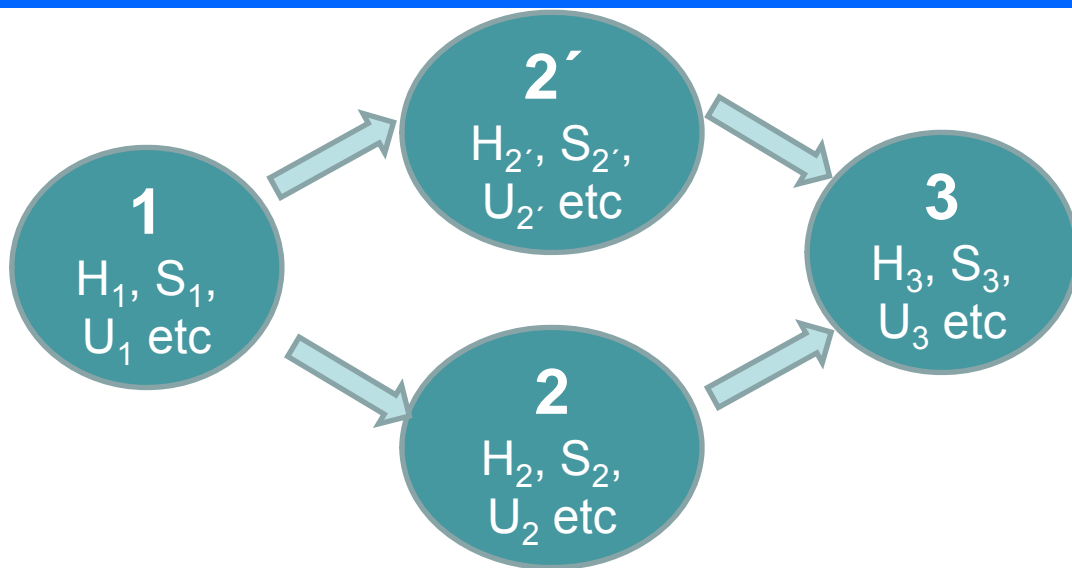- http://www.oup.com/uk/orc/bin/9780198700722/
- e-book:
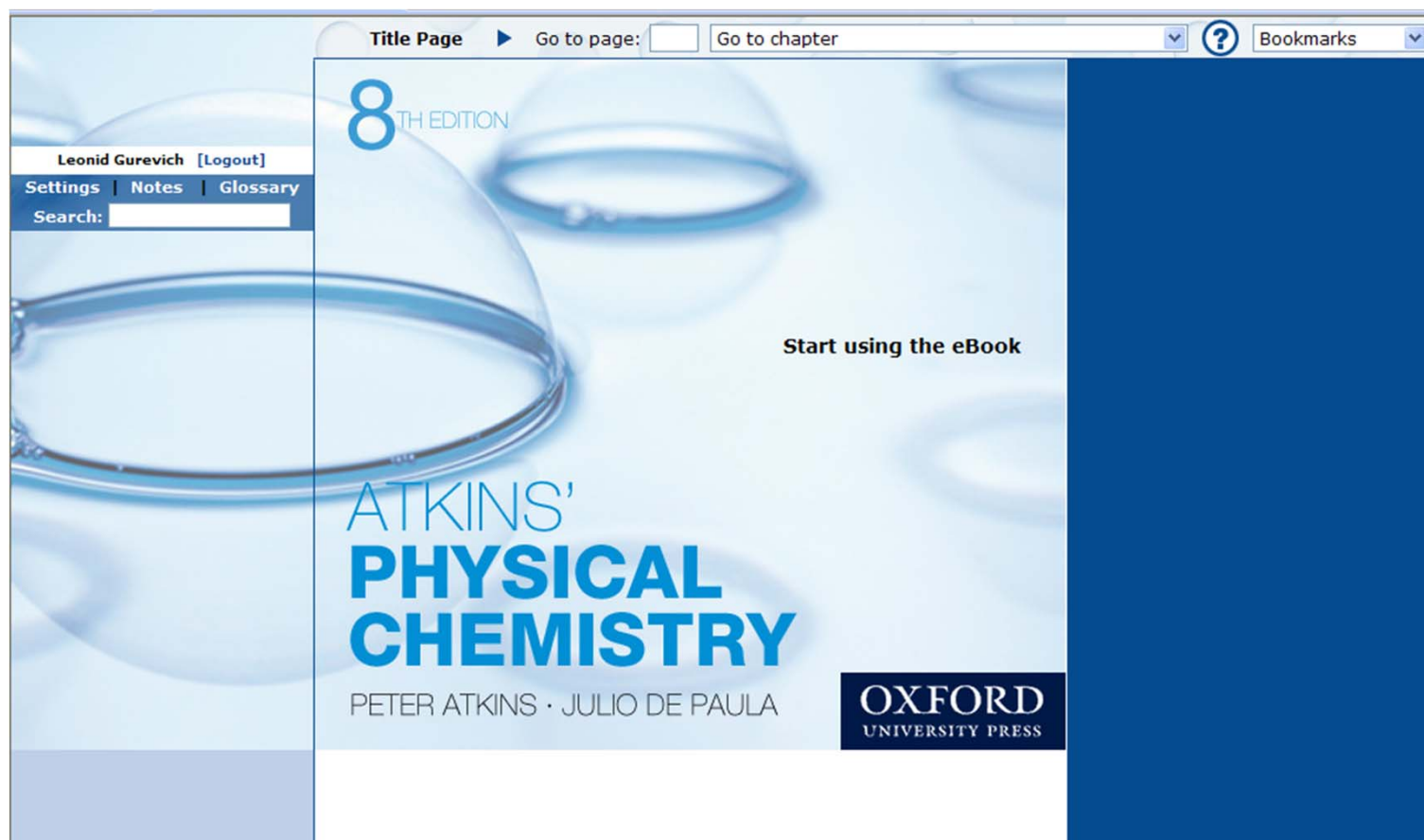
# Lecture 1
## *13-10-2008*

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

# Thermodynamic Functions



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

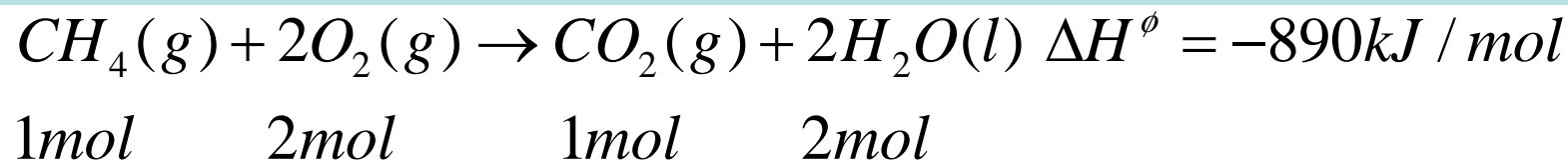$$\Delta U = U_f - U_i$$

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

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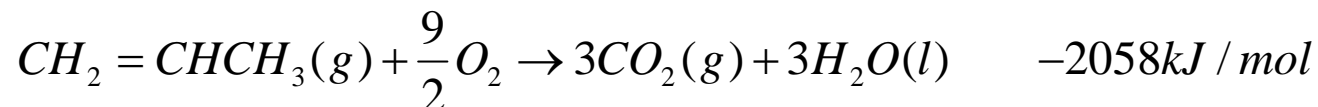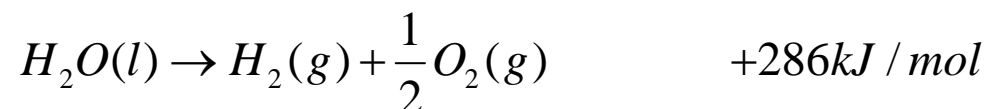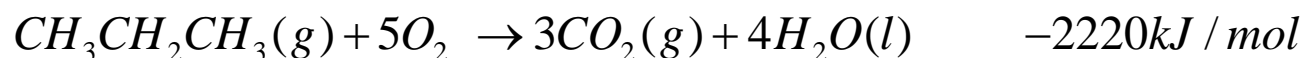
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H^{\phi} = -890 kJ/mol$$

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

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

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

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

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

- 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:

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

# Combining the First and Second Law

$$dU = dq + dw$$

For closed system in the absence of additional work

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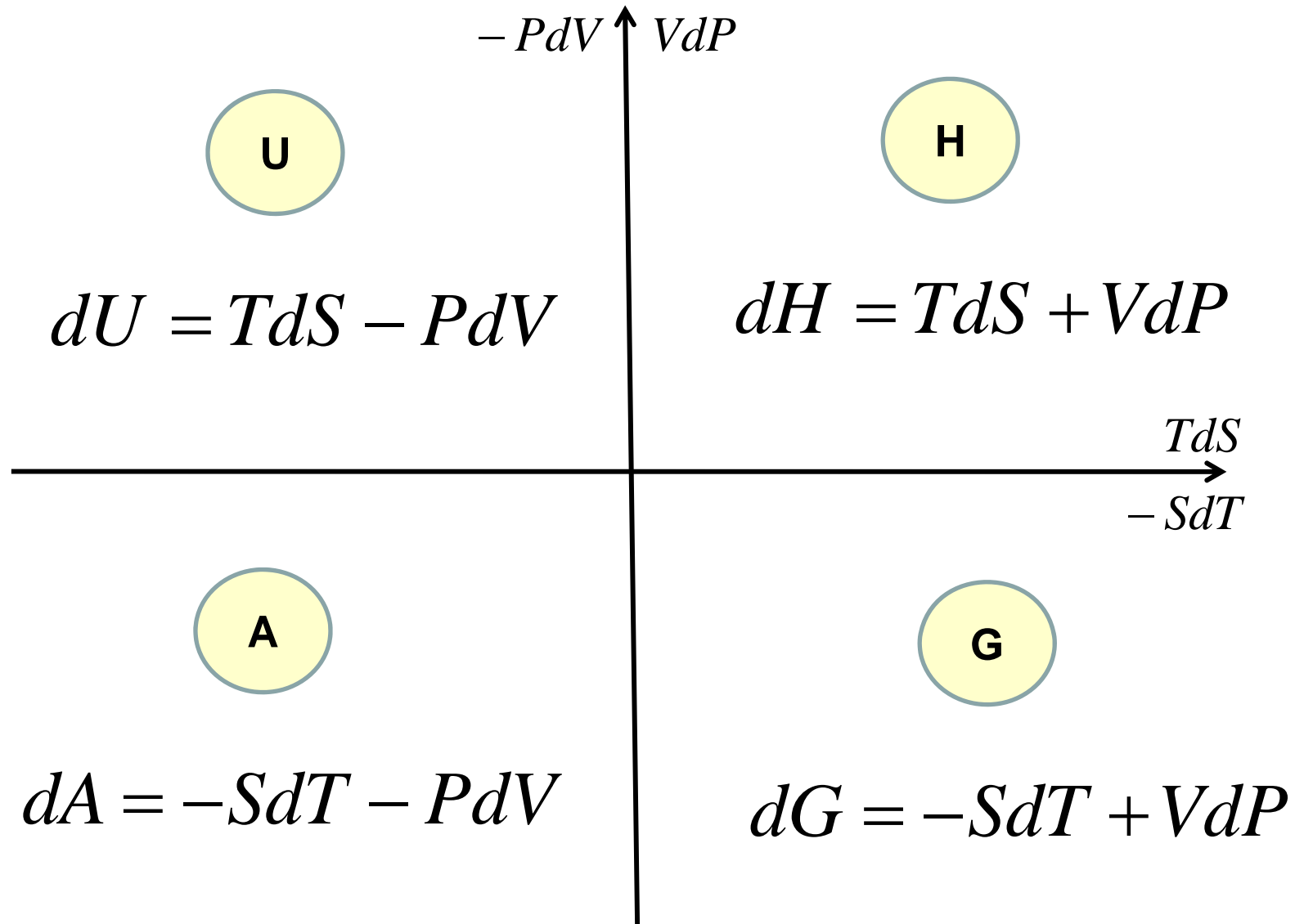
$$dU = TdS - pdV$$

**Fundamental equation**

Can be applied to reversible and irreversible changes

Mathematically:

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

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

# Differential form of thermodynamic functions



$-PdV$   $VdP$

$TdS$

$-SdT$

**U**

$$dU = TdS - PdV$$

**H**

$$dH = TdS + VdP$$

**A**

$$dA = -SdT - PdV$$

**G**

$$dG = -SdT + VdP$$

# Properties of Gibbs energy

$$G = H - TS$$
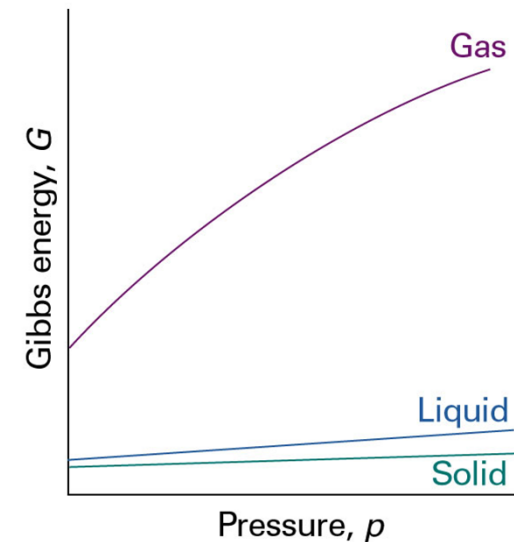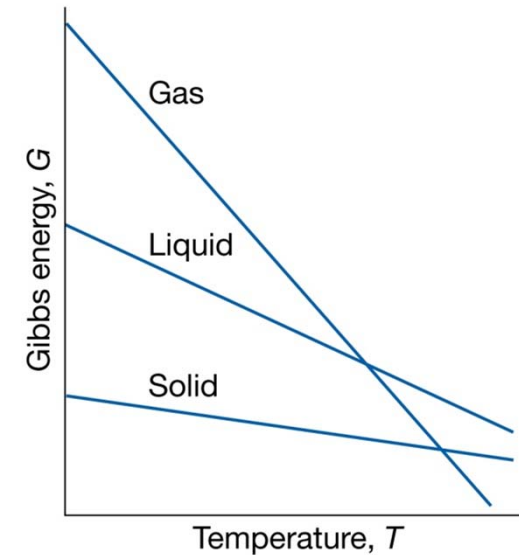
$$dG = -SdT + Vdp$$

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

- G decreases with temperature, proportional to entropy

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

# 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
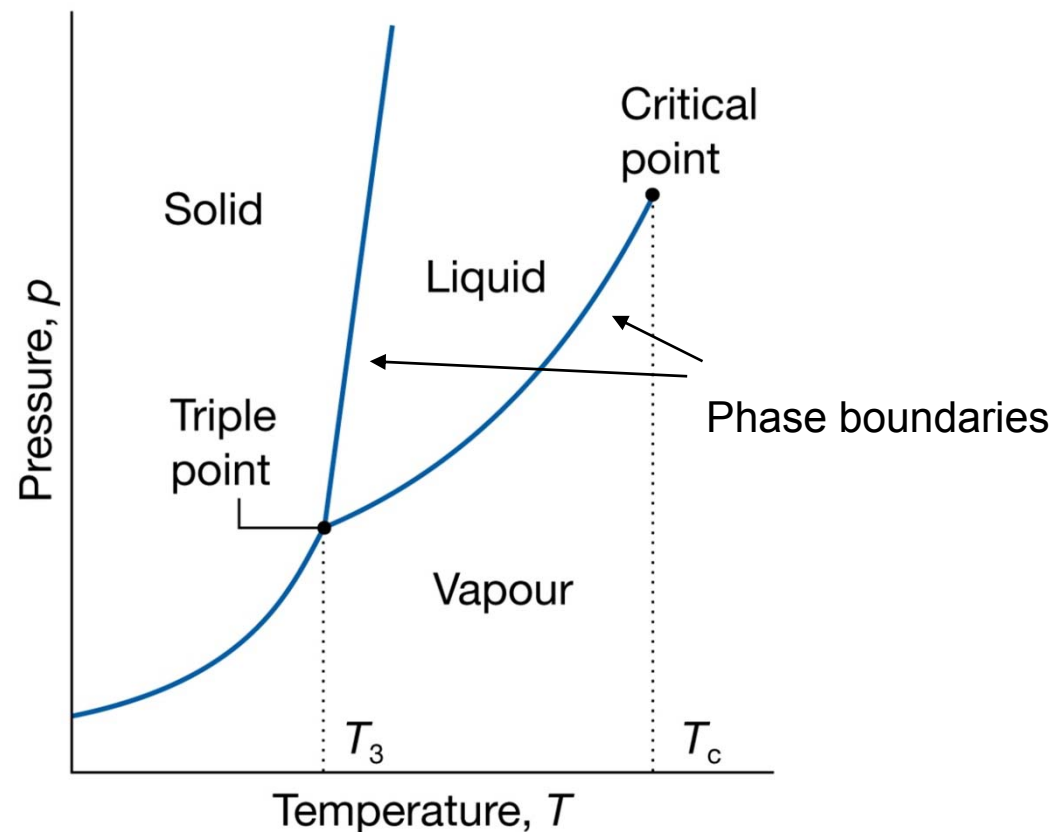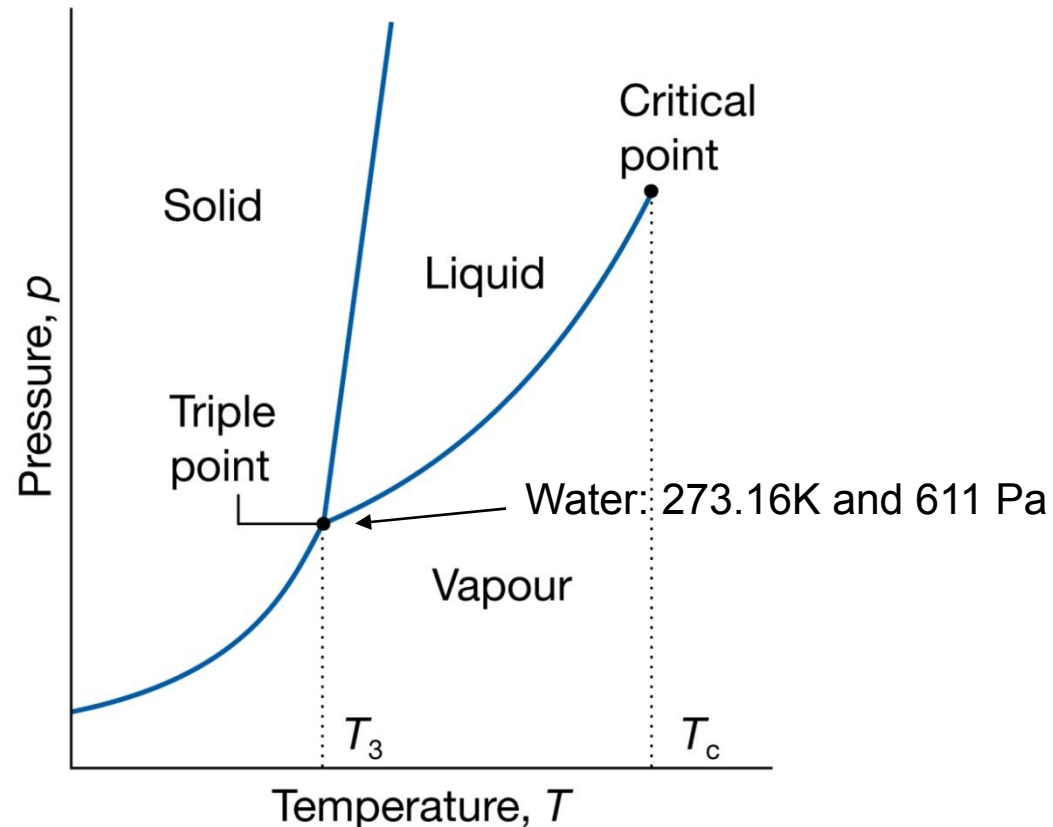
# Phase boundaries
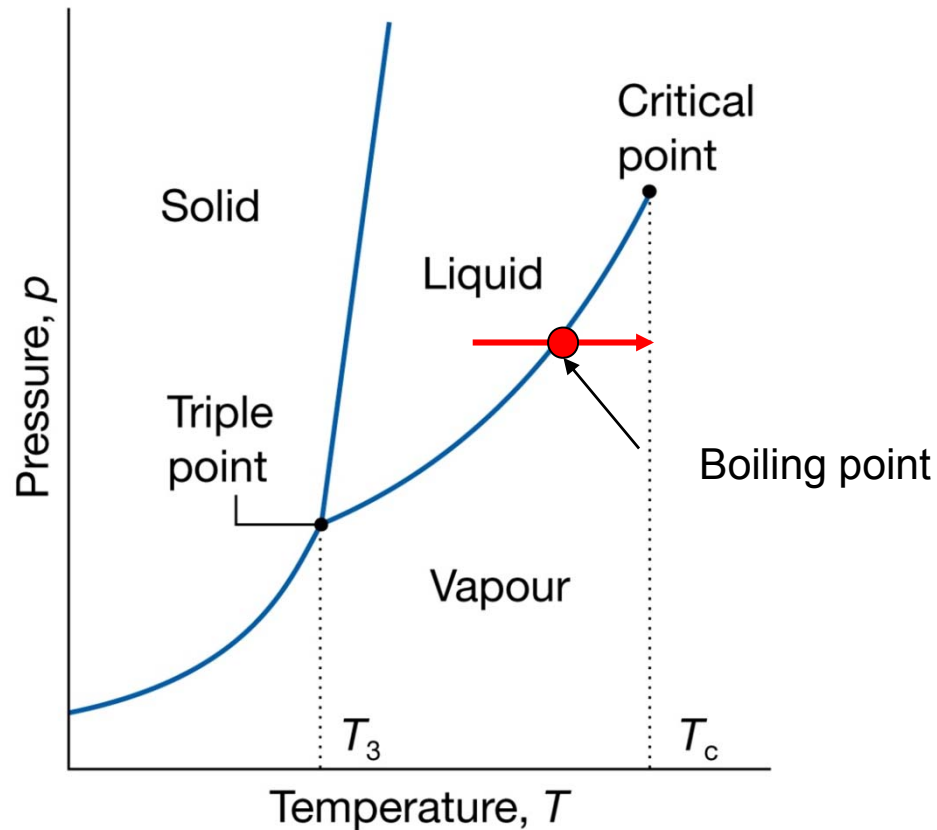


**Boiling temperature** – the temperature at which vapour pressure is equal to external pressure

**Standard** boiling temperature – the temperature where vapour pressure is 1 bar (0.987 atm).
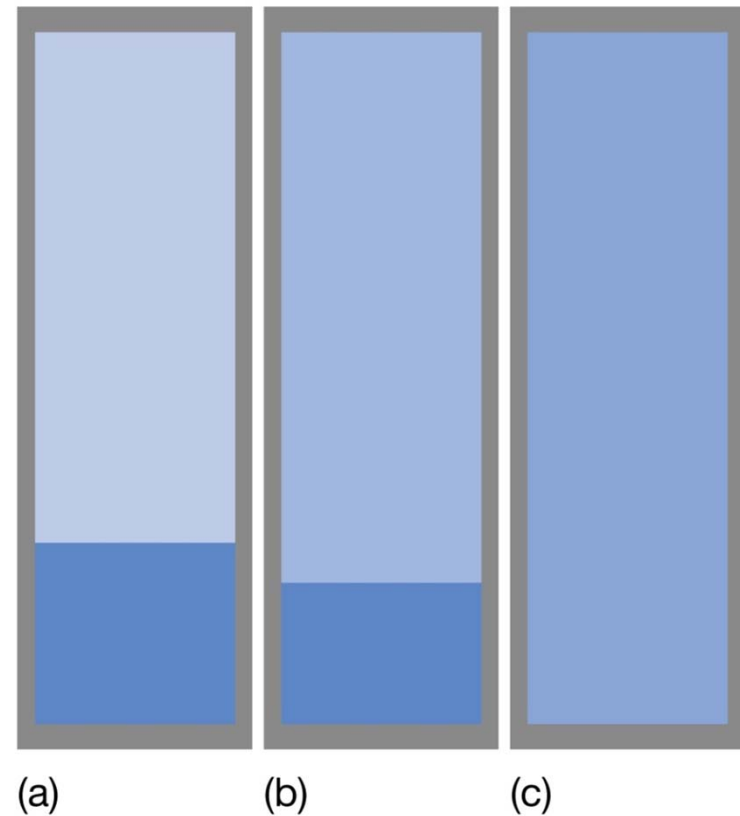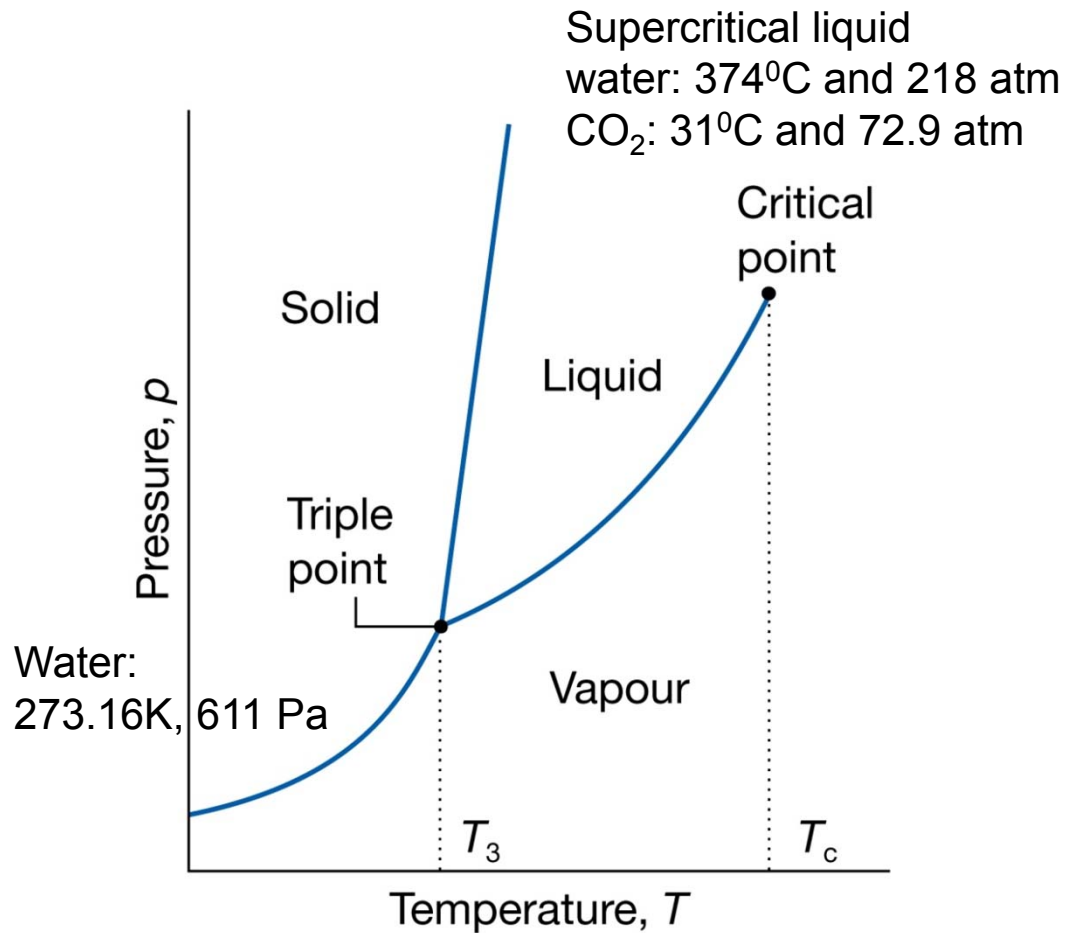
# Phase boundaries



**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 boundaries

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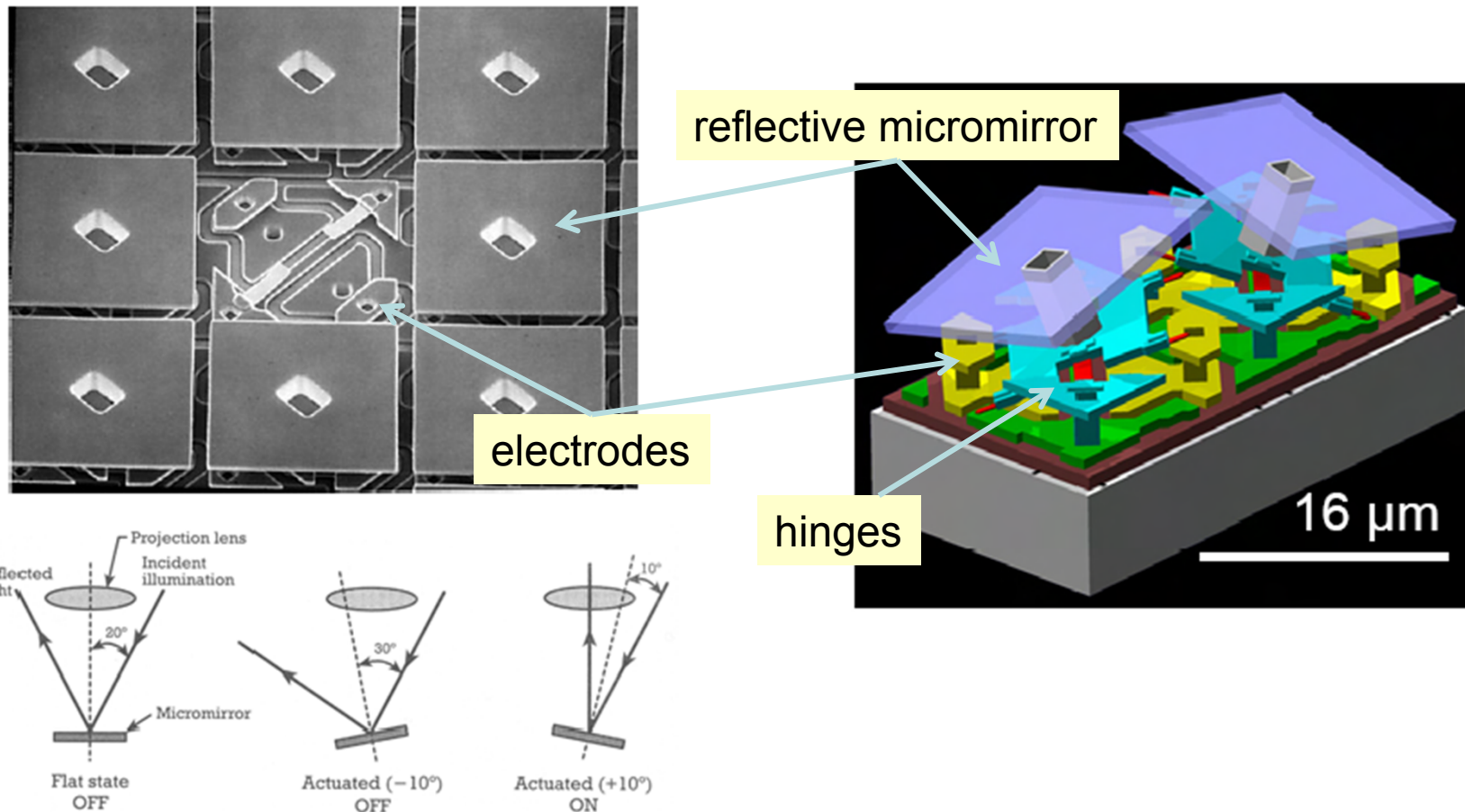water: $374^0C$ and 218 atm
$CO_2$: $31^0C$ and 72.9 atm



Heating liquid in a closed vessel

Applications: Supercritical drying; dry cleaning; supercritical fluid chromatography

# MEMS free-standing structures

- Texas Instrument DLP micromirror array



reflective micromirror

electrodes

hinges

16 µm

Projection lens
Incident illumination
Reflected light

20°

Micromirror

Flat state
OFF

30°

Actuated (−10°)
OFF

10°

Actuated (+10°)
ON

# Supercritical drying in nanofabrication

- Surface tension at a liquid-air interface can destroy free standing micro/nanostructures
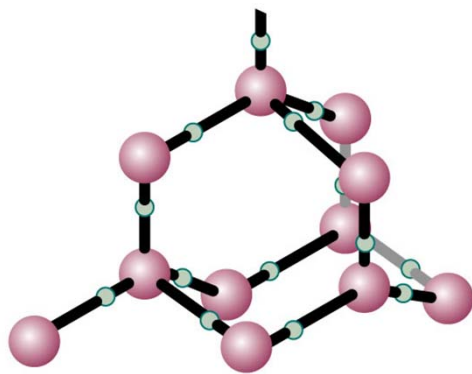


permanent sticking
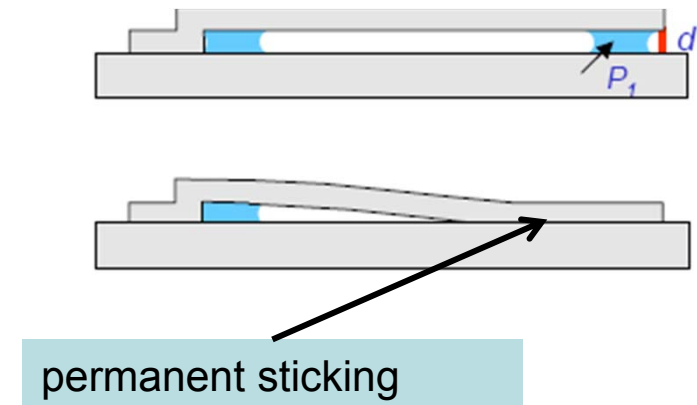
- Typical supercritical $CO_2$ drying steps:
    - sacrificial layer etching and structure release in HF
    - thorough rinse with water
    - water displaced with methanol
    - methanol displaced with $CO_2$ liquid
    - $CO_2$ is evaporated via supercritical path
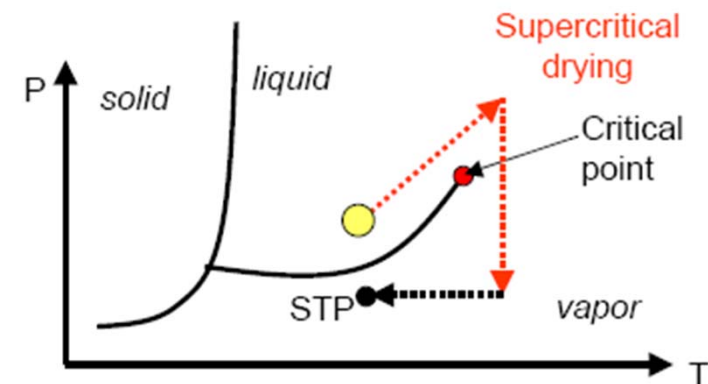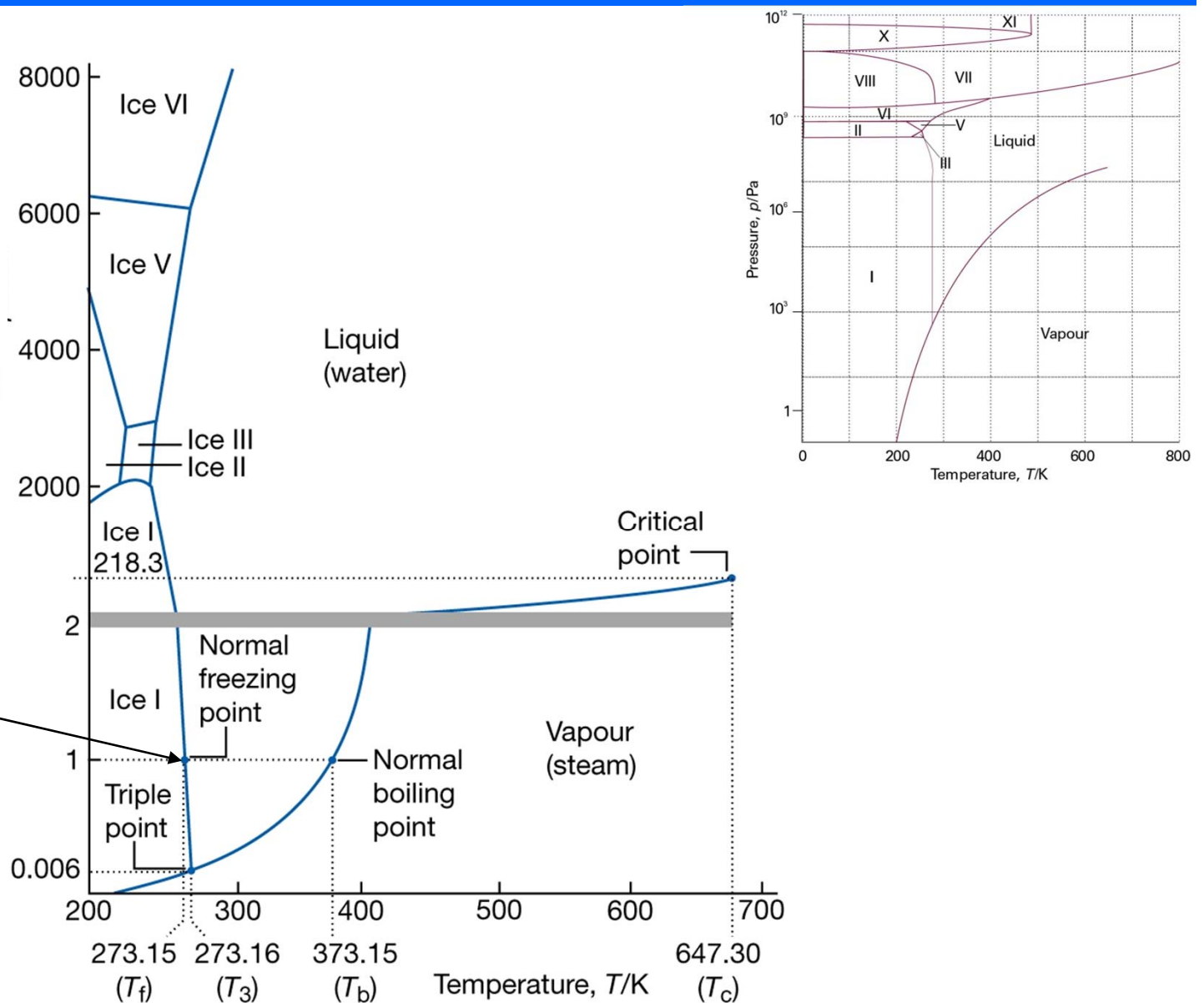
# Phase diagrams: $CO_2$
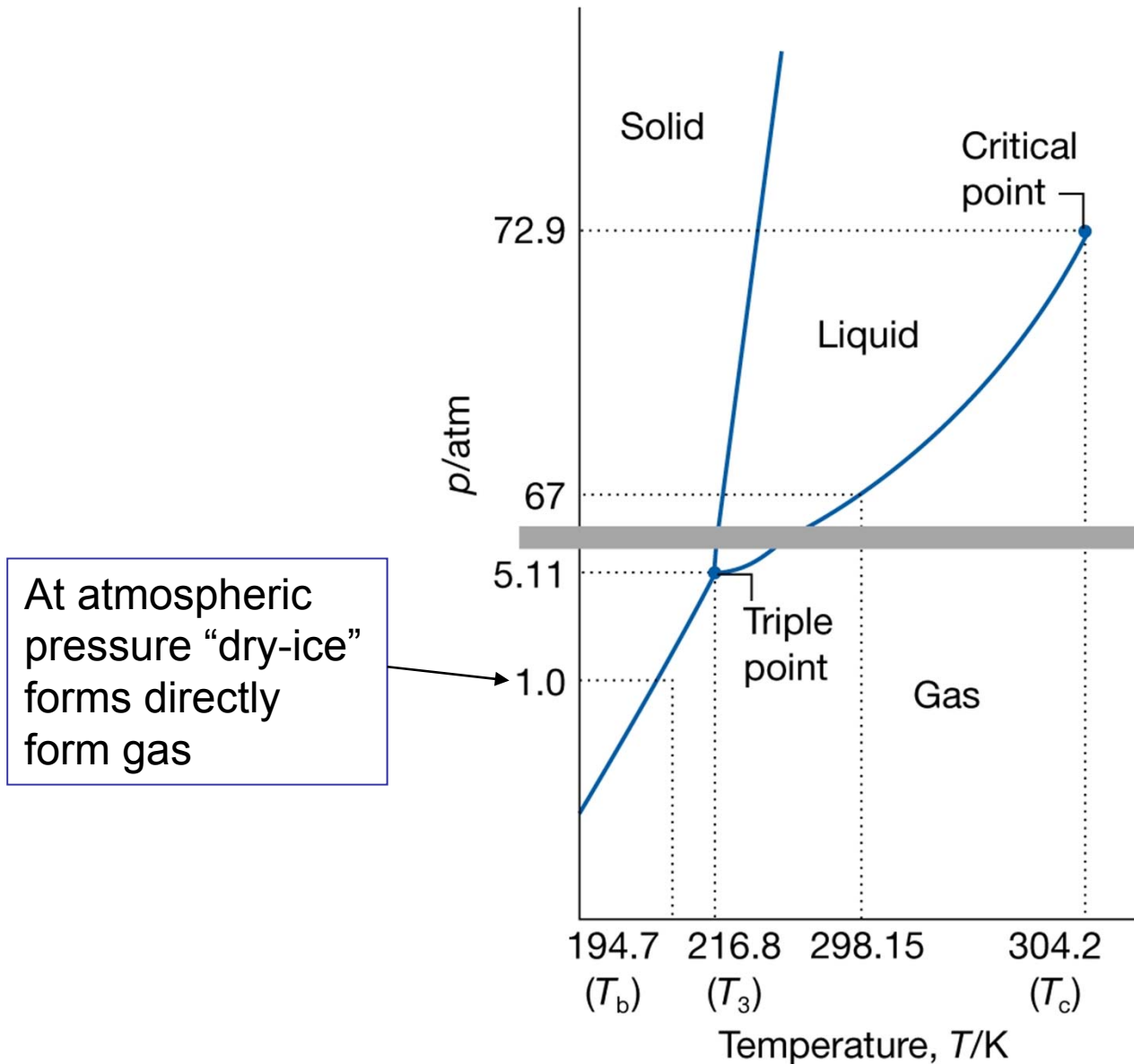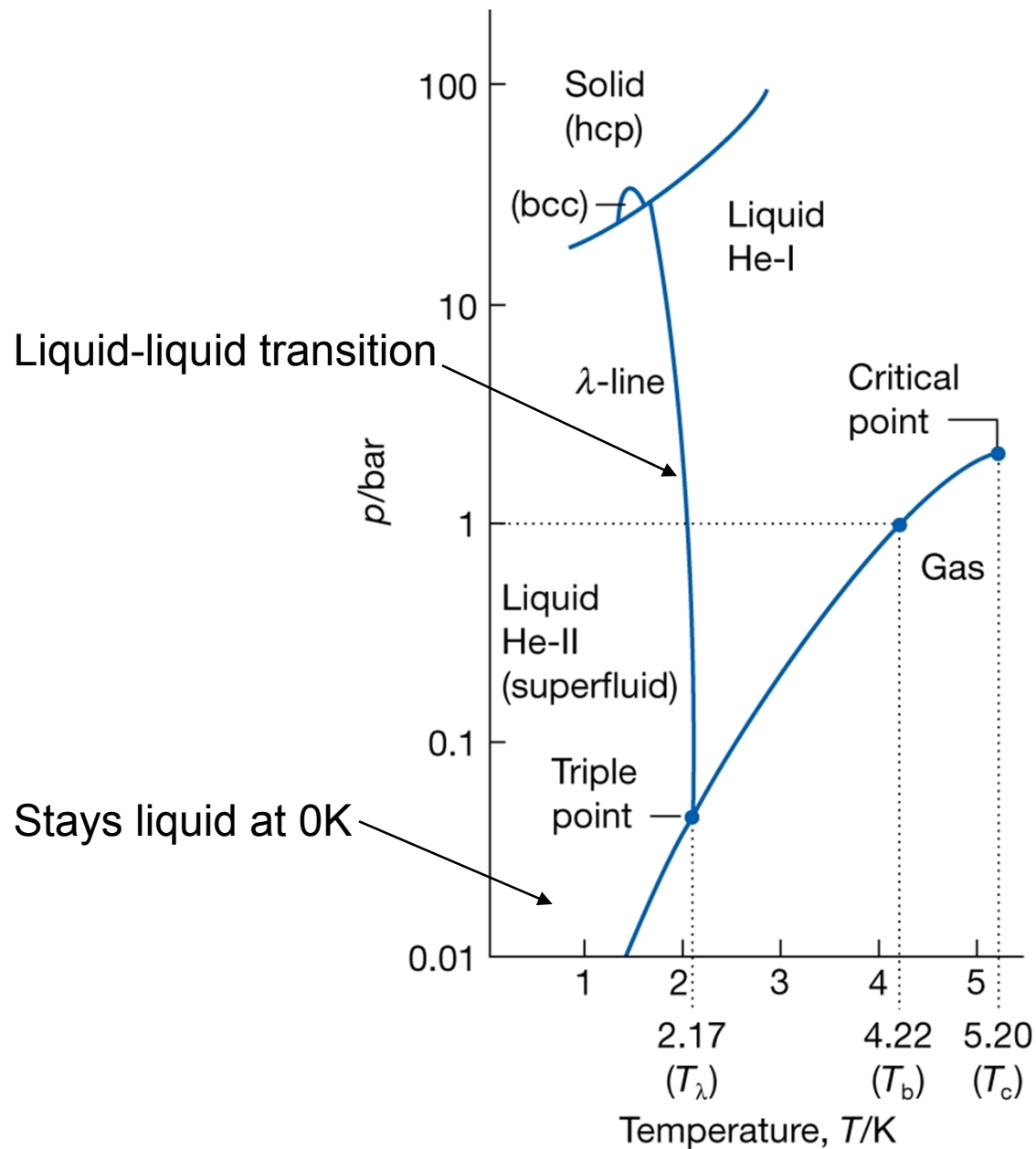
# Phase diagrams: water



Ice-I structure

Negative slope

# Phase diagrams: $^4$He

# 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 $\mu_1$ and exchange material from there with another place at chemical potential $\mu_2$.

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

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

Same chemical potential
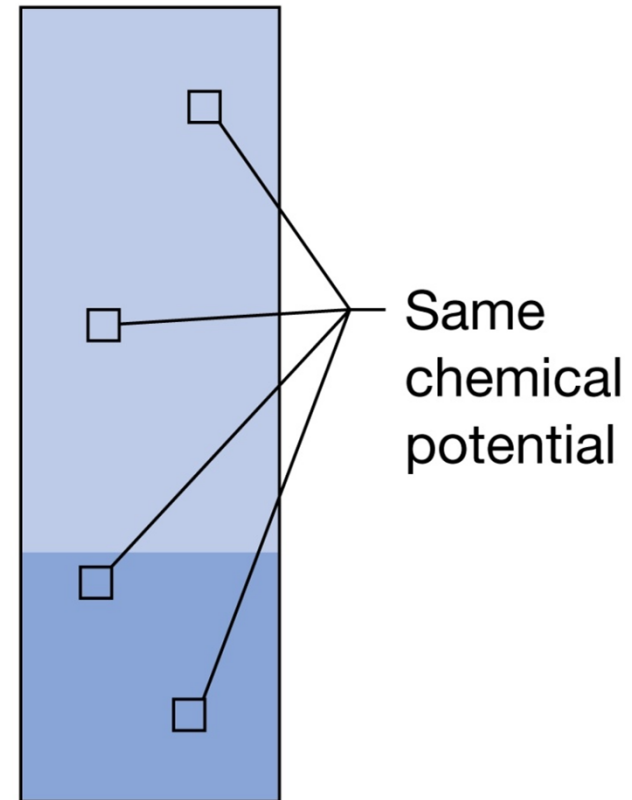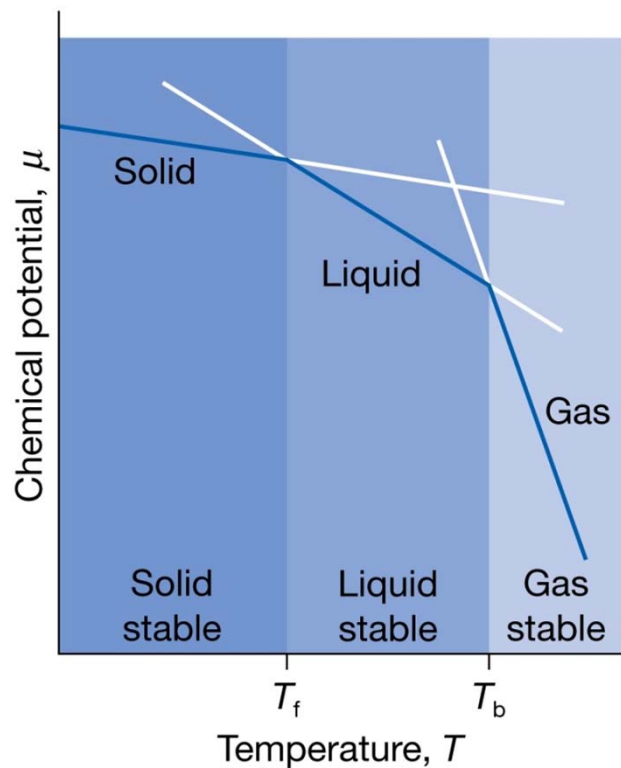
# Phase transitions

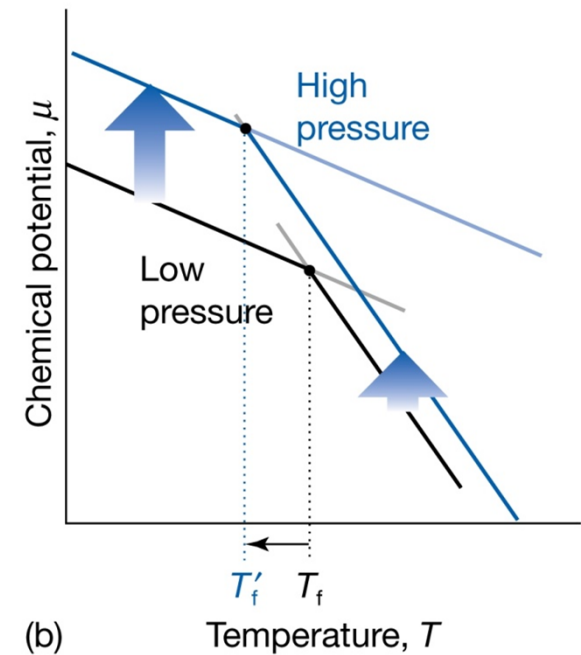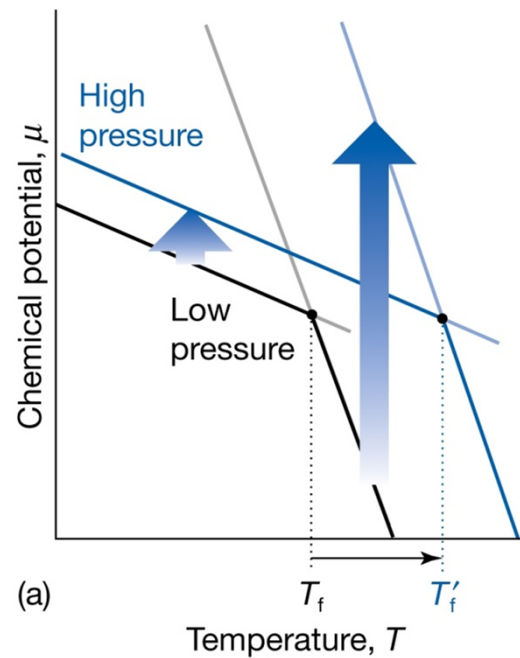$$dG = -SdT + Vdp, \quad \mu = G_m$$

## Temperature dependence

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

## Melting point vs. applied pressure

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

# The effect of applied pressure on vapour pressure

What happens with the liquid-vapour equilibrium when the pressure is applied selectively to liquid?

• when pressure applied to a condensed phase its vapour pressure rises: the molecules are 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

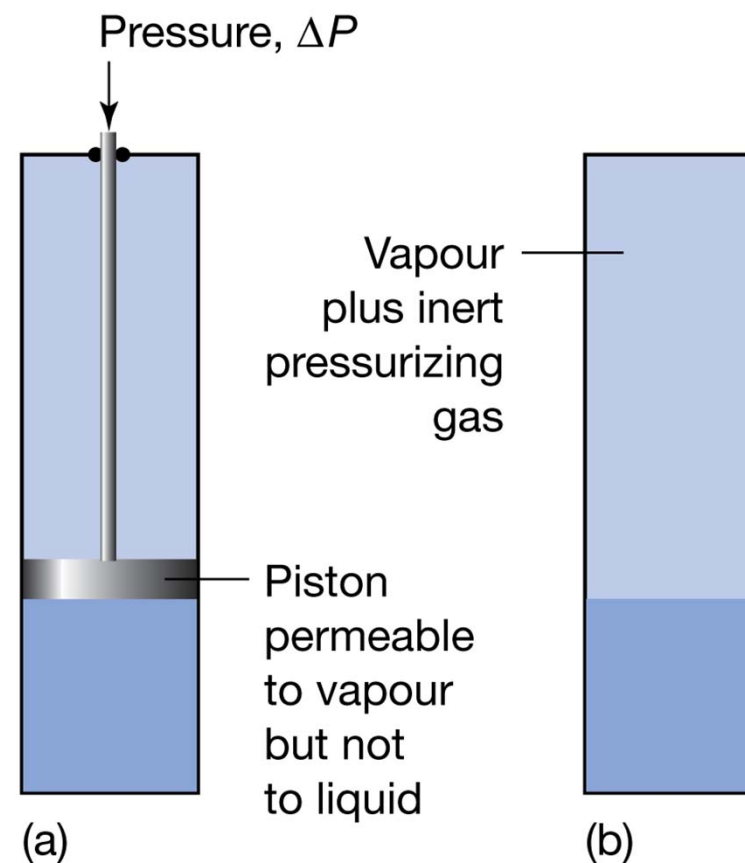Pressure, $\Delta P$

Indeed:

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

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

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

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

Vapour plus inert pressurizing gas

Piston permeable to vapour but not to liquid

(a)

(b)

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

# Location of phase boundaries
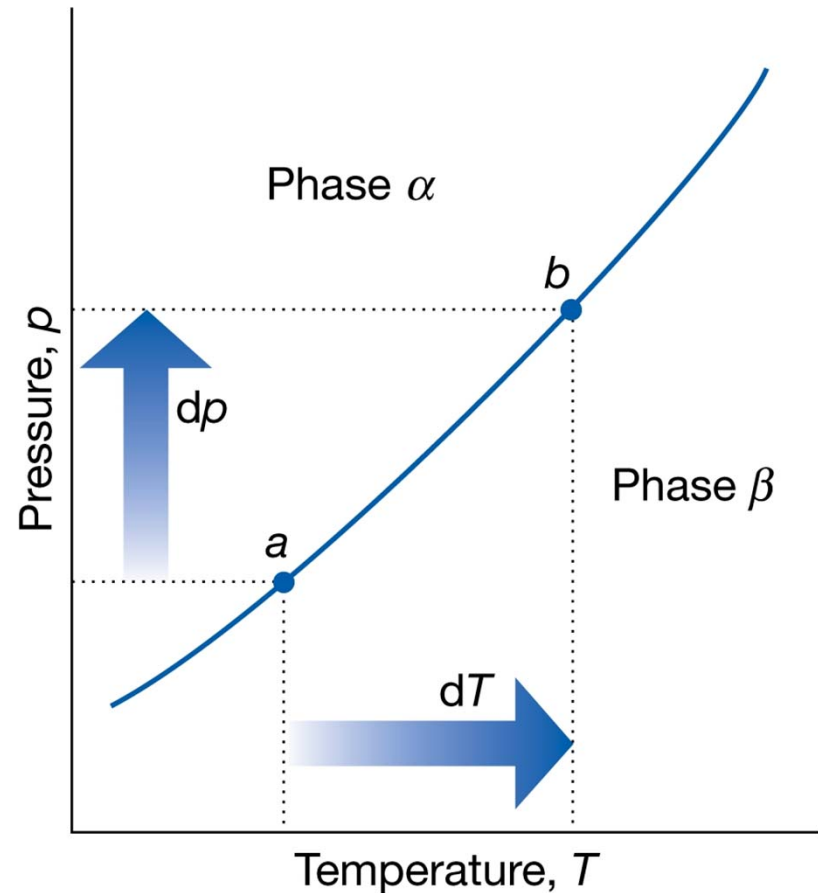
$$\mu_{\alpha}(p,T) = \mu_{\beta}(p,T)$$

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

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

Clapeyron equation:

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



Phase $\alpha$

Phase $\beta$

dp

dT

Pressure, $p$

Temperature, $T$

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

# Location of phase boundaries

**Solid-liquid boundary**

usually>0

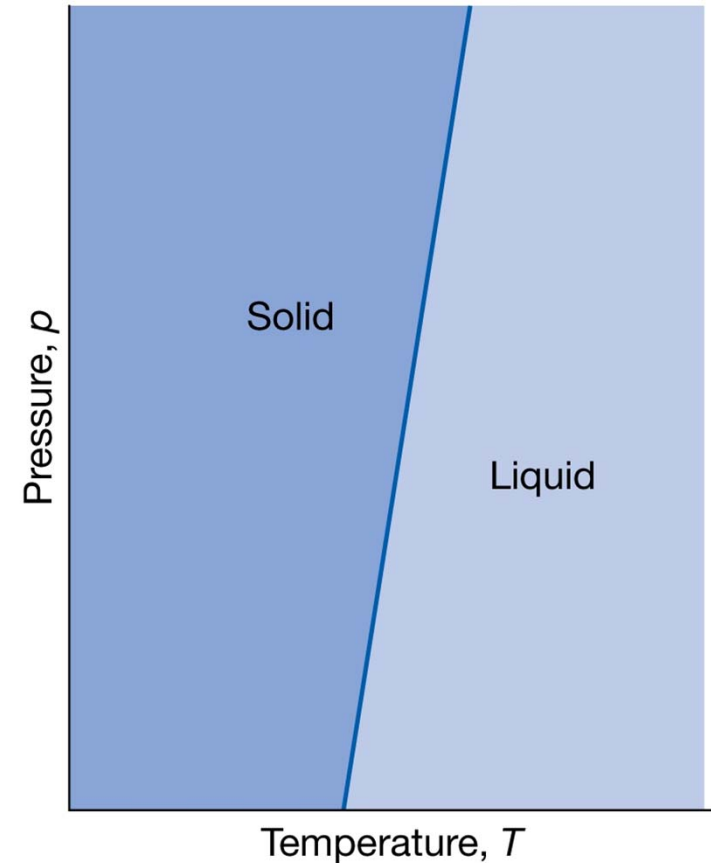$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$$

usually>0 and small

assuming $\Delta_{fus}H$ and $\Delta_{fus}V$ =const:

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

approximate equation for liquid solid boundary:

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

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

Pressure, $p$

Solid

Liquid

Temperature, $T$

# Location of phase boundaries

**Liquid-vapour boundary**

usually>0 and large

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$
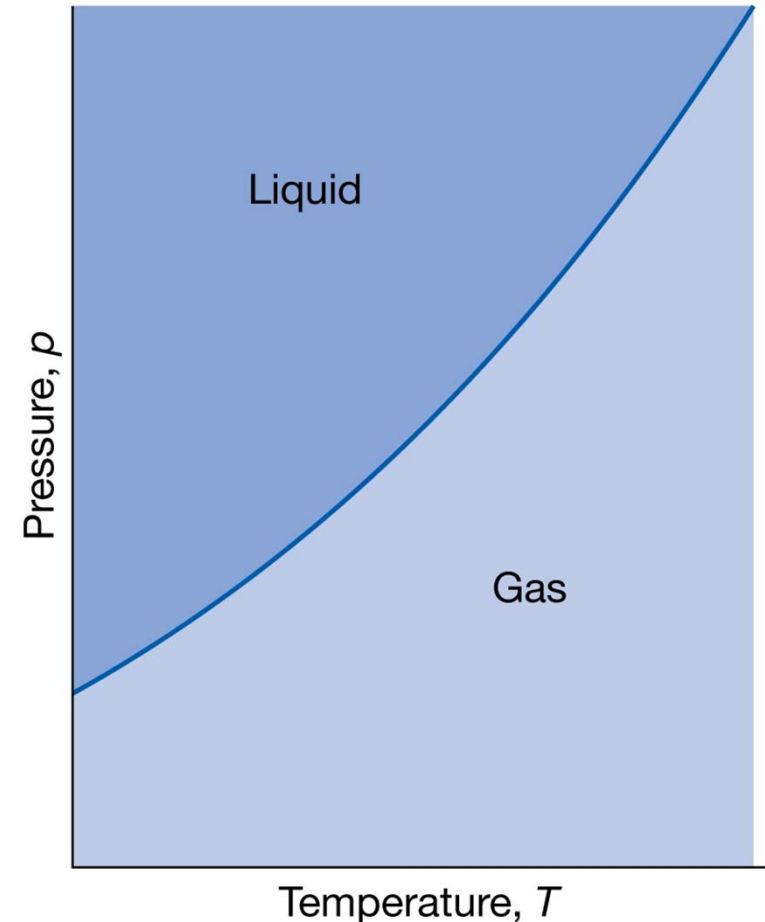
usually>0 and large

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

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

Clausius-Clapeyron equation

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

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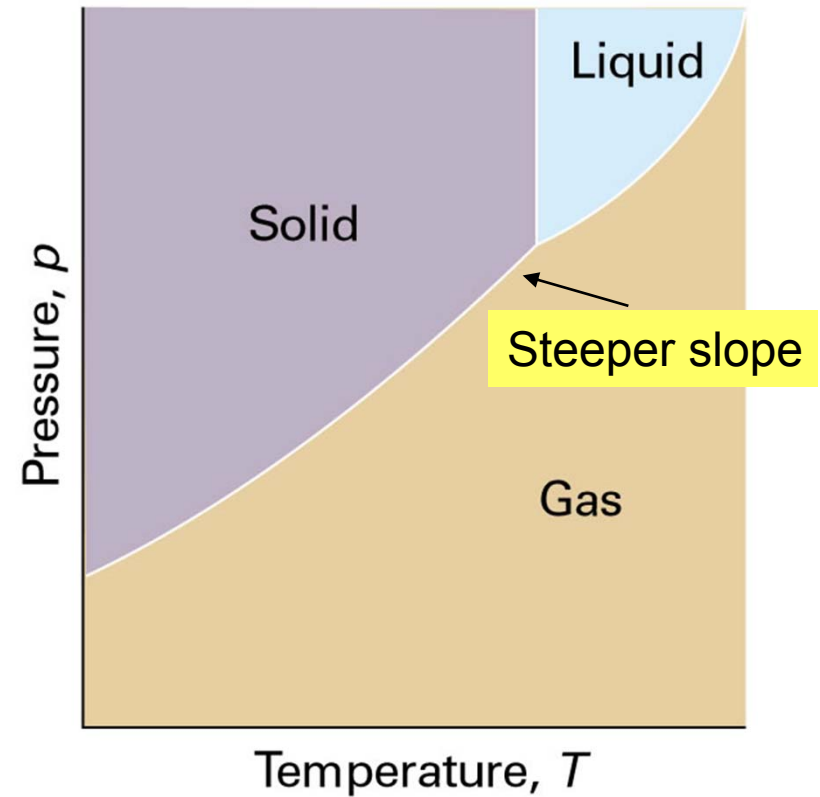
# Location of phase boundaries

**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
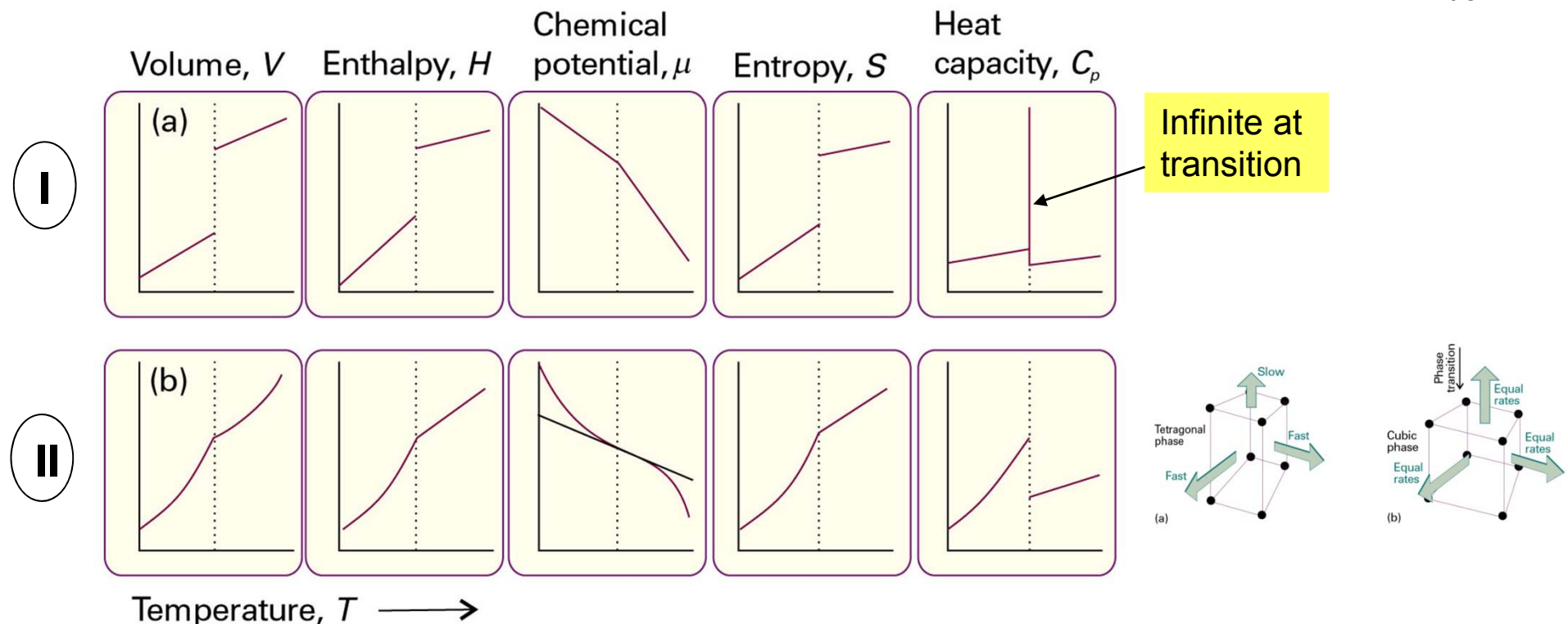
# Phase Transitions

| 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

Smooth transition



**A**

**B**
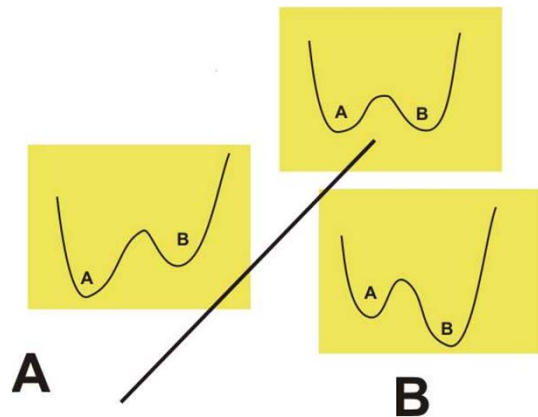
Overcooling/overheating is possible

Example: XY-ferromagnet

Order parameter: local magnetization

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

# Problems

- **4.6a:** By how much does the chemical potential of copper change when pressure is increased from 100kPa to 10 MPa ?

- **4.14a**: 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.)

- **4.16a** 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$^{-3}$.

- **4.17a** What fraction of the enthalpy of vaporization of water is spent on expanding water vapour

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