Chapter 4.

Real Materials + 1 Component

Physical Transformations of Pure Substances

The Stability of Phases

Basic Principle:

The tendency of systems slides down to lower chemical potential.

The principle of **uniform chemical potential** applies.

However, **many phases can be in equilibrium**.

Temperature dependence of phase stability

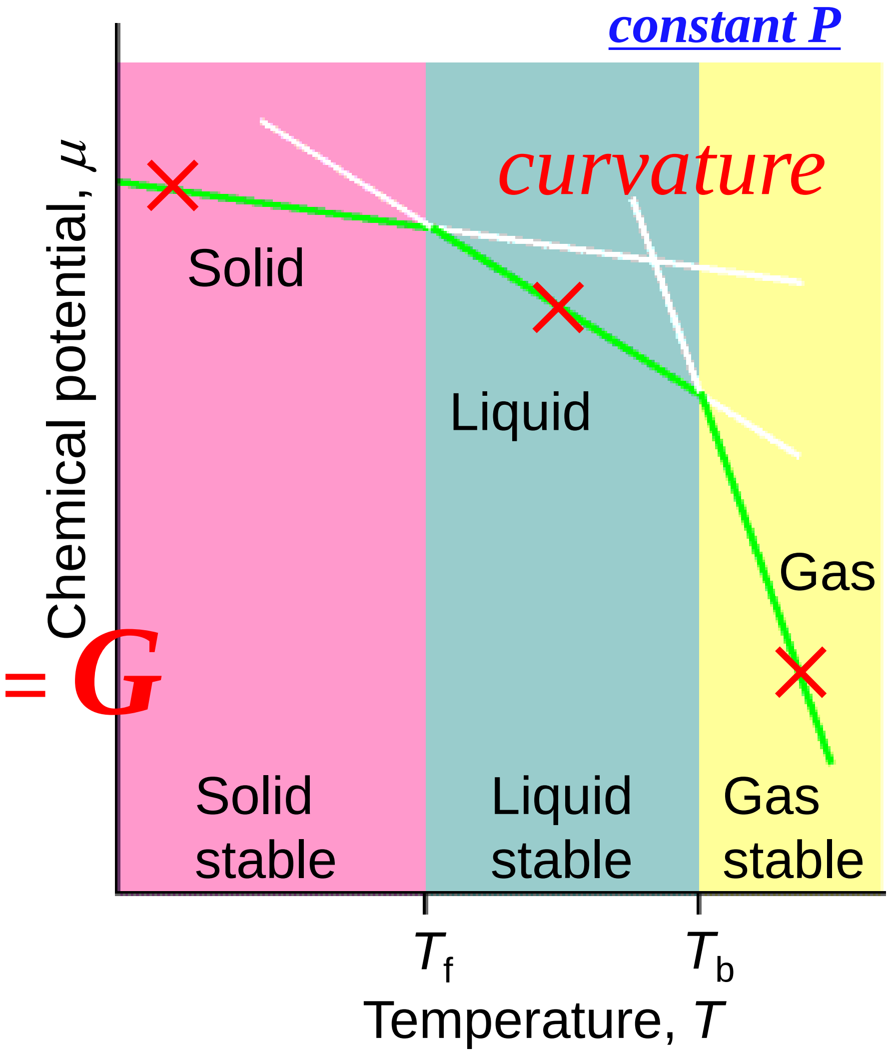
$\mu(s)$, $\mu(l)$, $\mu(g)$: the chemical potentials of the solids, liquids, and gas phases.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \qquad \left(\frac{\partial G_m}{\partial T}\right)_p = \left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

As T rises, the chemical potential falls because **S_m is always positive**.

The gradient is steeper for gases than for liquids ($S_m(g) > S_m(l)$), and steeper for a liquid than the solid ($S_m(l) > S_m(s)$).

Pure Substance



The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance.

The lines should be curved.

The phase with the lowest chemical potential at the specified *T* and *P* is the most stable.

The transition temperatures, the melting and boiling temperatures, are the temperatures at which **the chemical potentials of two phases are equal**.

The chemical potentials of two phases are equal in multicomponents:

$$\mu_{Li}^{\alpha} = \mu_{Li}^{\beta}$$

$$\mu_{Si}^{\alpha} = \mu_{Si}^{\beta}$$

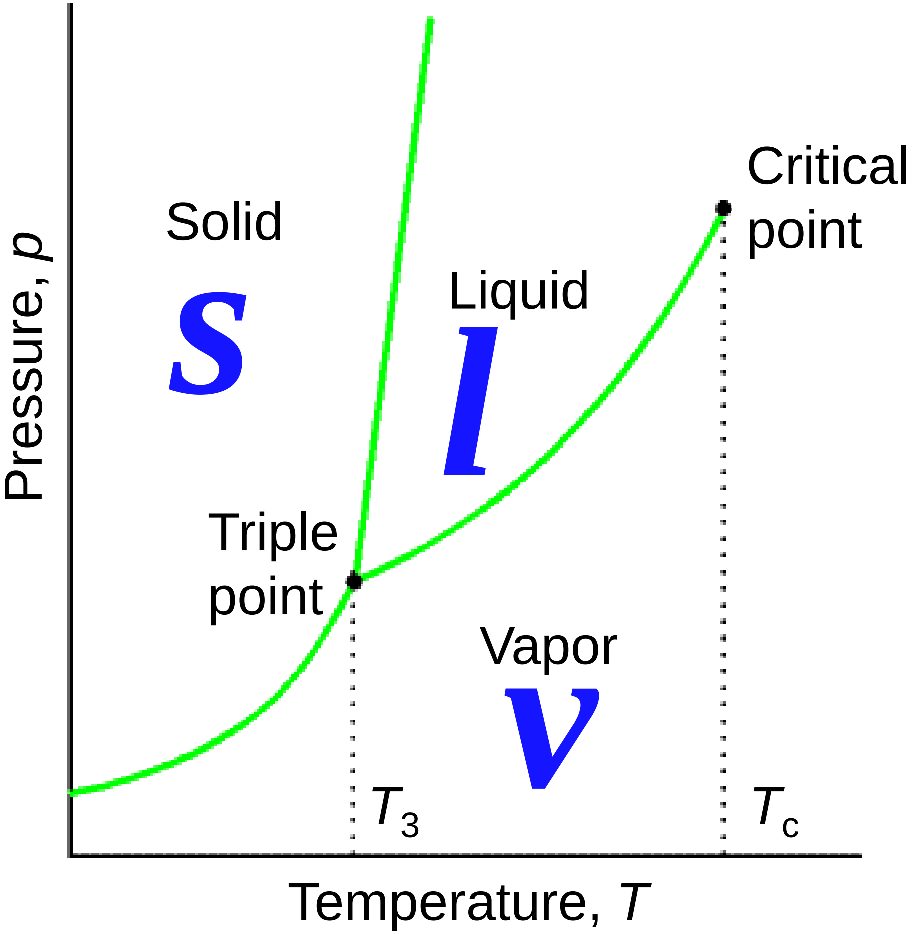


Figure 4A.4

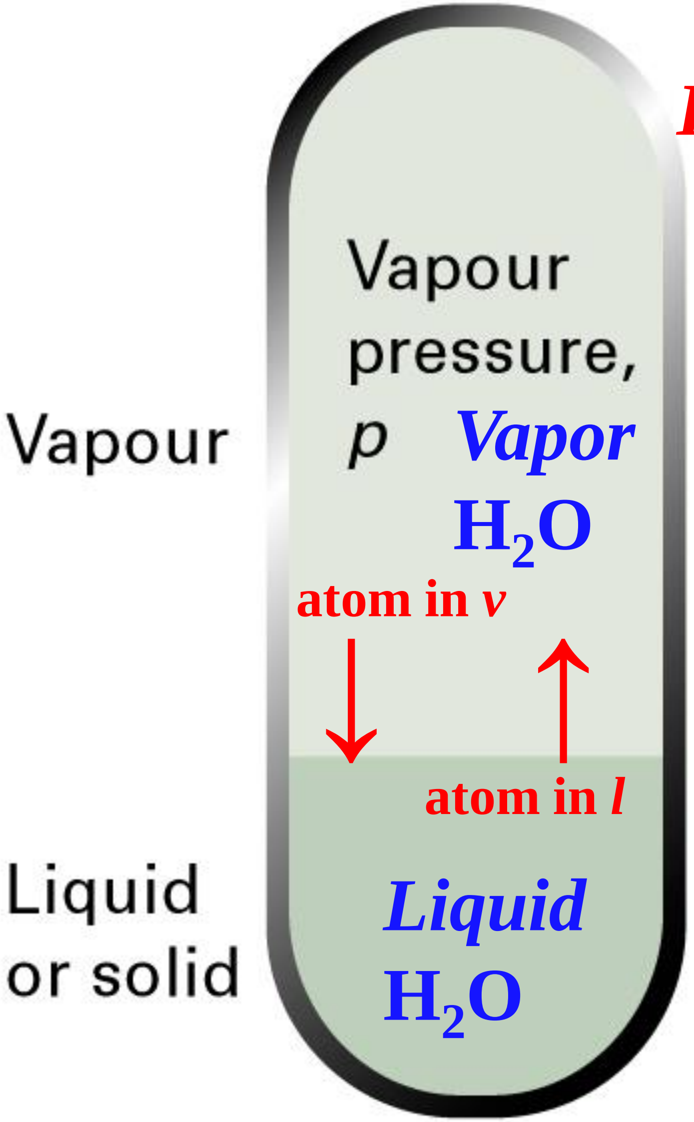
The general regions of pressure and temperature where solid, liquid, or gas is stable (that has the lowest chemical potential).

The solid phase is the most stable phase at low temperatures and high pressures.

Uniform Chemical Potential

Only 1 Component

In Equilibrium



Vapor H_2O

atom in *v*

atom in *l*

Liquid H_2O

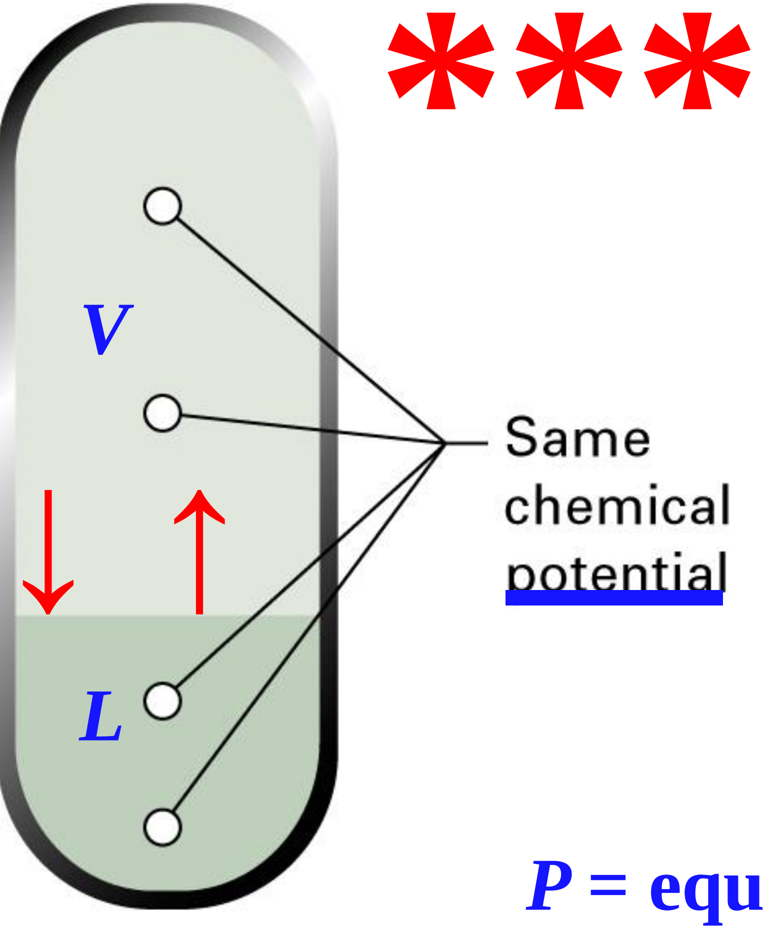
Figure 4A.3

The vapor pressure of a liquid or solid is the pressure exerted by the vapor in equilibrium with the condensed (*L* or *S*) phase.

$T < T_{melting}$ **300 K with Ar at 1 atm**

In general, Au (*materials*) and air (*or pure nitrogen*).

Only 1 Component



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When **two or more phases are in equilibrium**,

Chemical potential of a component is

the same in each phase, and is the same at all points in each phase.

***P* = equilibrium vapor pressure**

$\Delta G = 0$

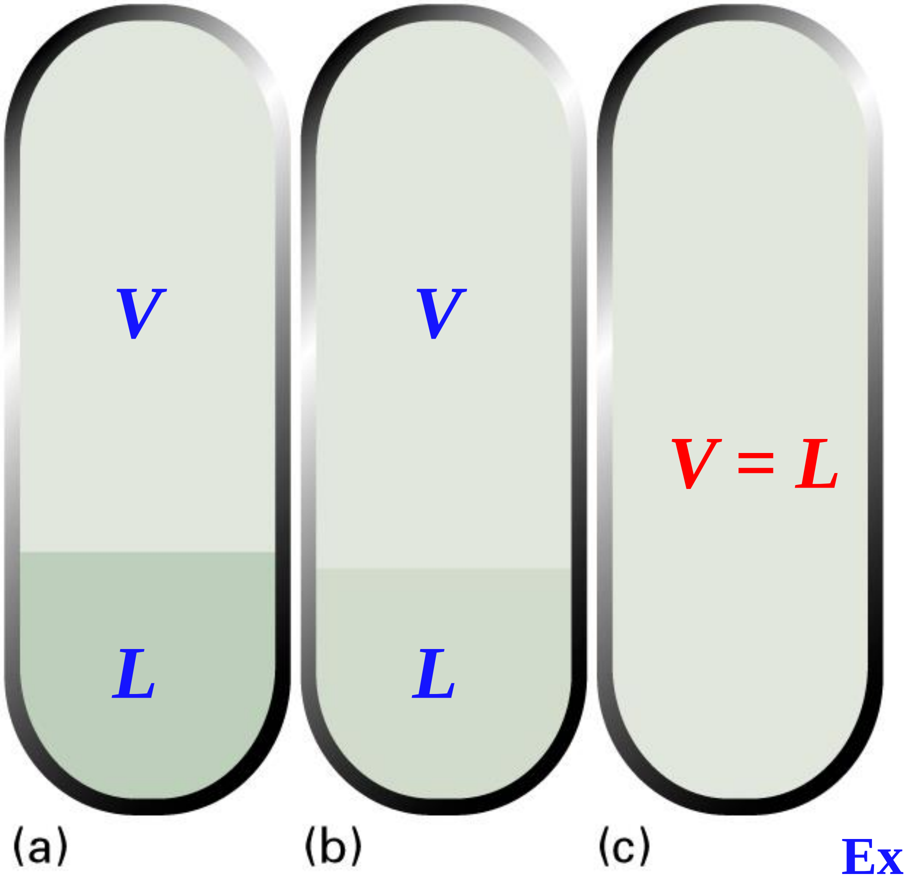
Only 1 Component

$T < T_c$

$P < P_c$

$T > T_c$

$P > P_c$



$T + P$ going up

Figure 4A.6

(a) A liquid in equilibrium with its vapor.

(b) When a liquid is heated in a sealed container, the fraction of vapor phase increases and that of liquid decreases slightly.

(c) There comes a stage at which the two densities are equal, and the interface between the fluids disappears.

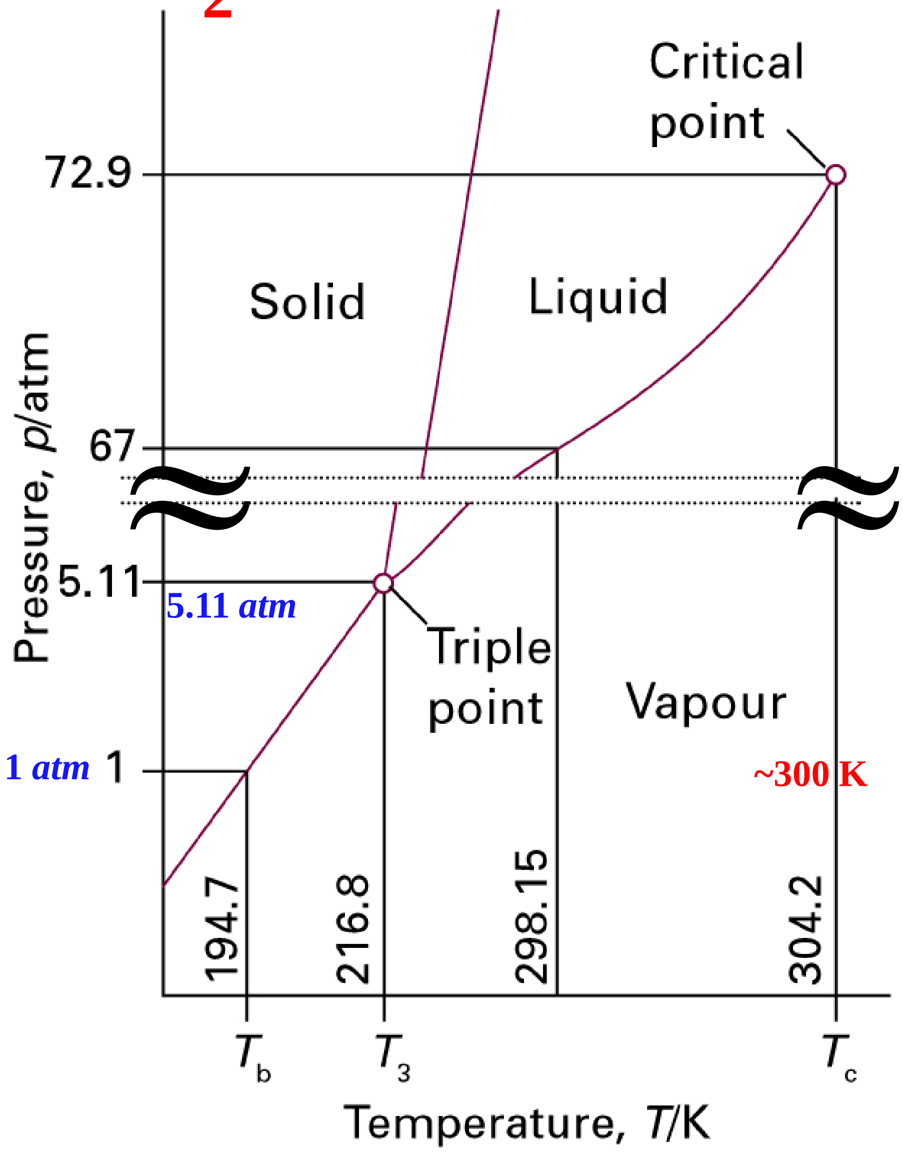
The container needs to be strong: the critical temperature of water is 374°C and the vapor pressure is then 218 *atm*.

Example:

continuous heating (constant volume)

CO_2

with Ar (or air) for the desired pressure



Phase diagram for carbon dioxide.

As the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions

A pressure of at least 5.11 *atm* must be applied.

Dry ice

- Baskin Robbins (ice cream)
- chemistry department

H_2O

+ Many Metastable Ice Phases

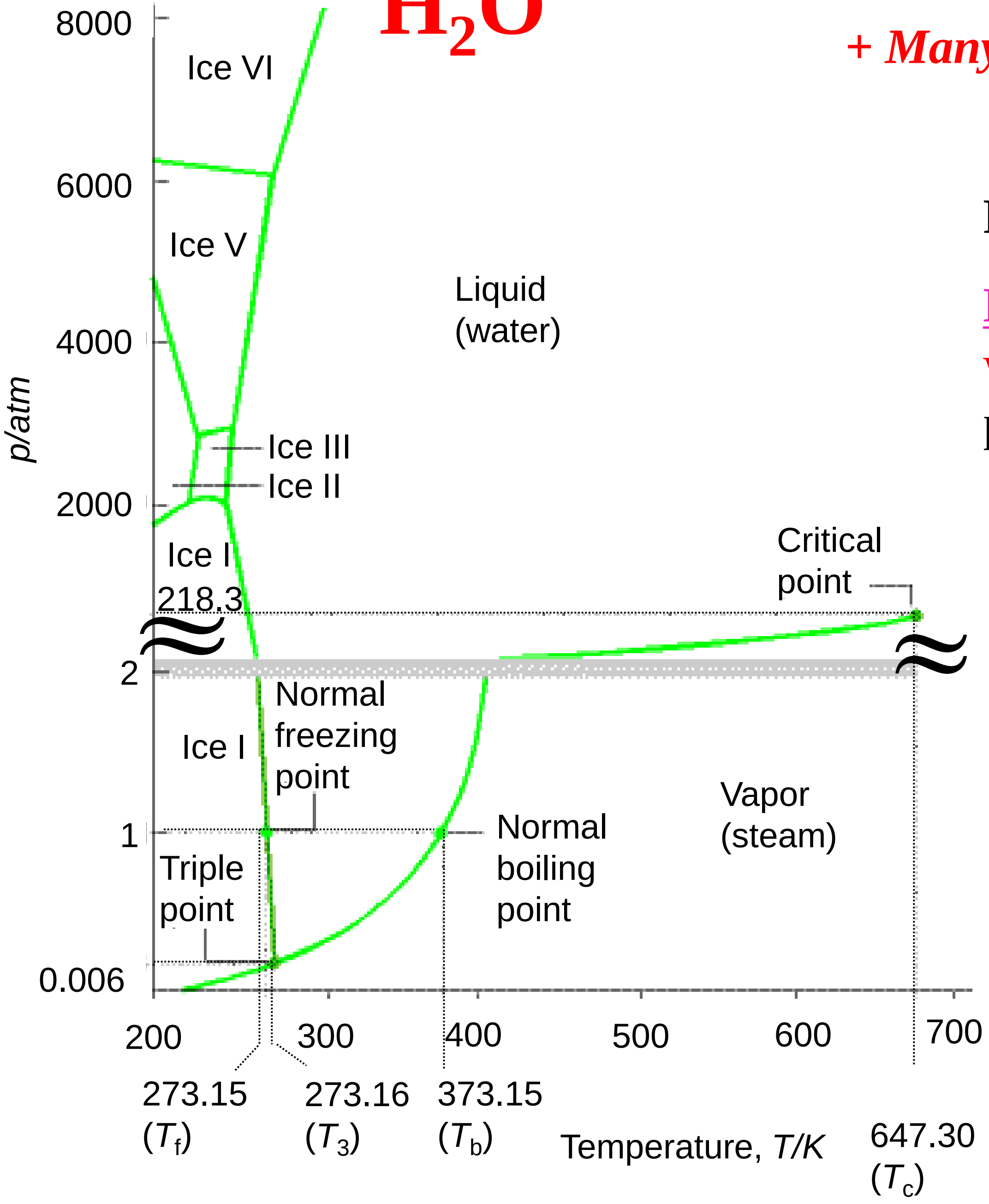
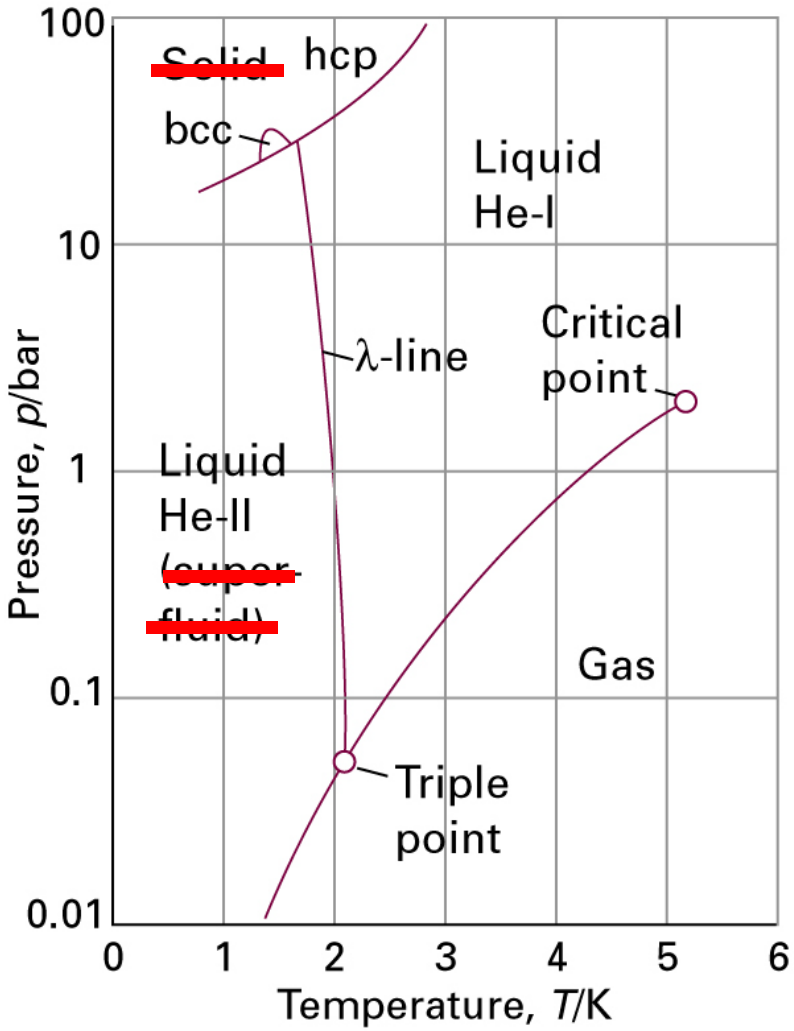


Figure 4A.9

Equilibrium Phase Diagram for water showing the different solid phases of ice.

He



~2 K

Figure 4A.11

The phase diagram for helium (^{4}He).

The λ-line marks the conditions under which the two liquid phases are in equilibrium.

Helium-II is the superfluid phase.

Note that a pressure of over 20 bar must be exerted before **solid helium** can be obtained.

Different solid phases:

hcp: hexagonal close packing
bcc: body-centered cubic

4B.1(b). Chemical Potential Dependence on Pressure

Pure Substances

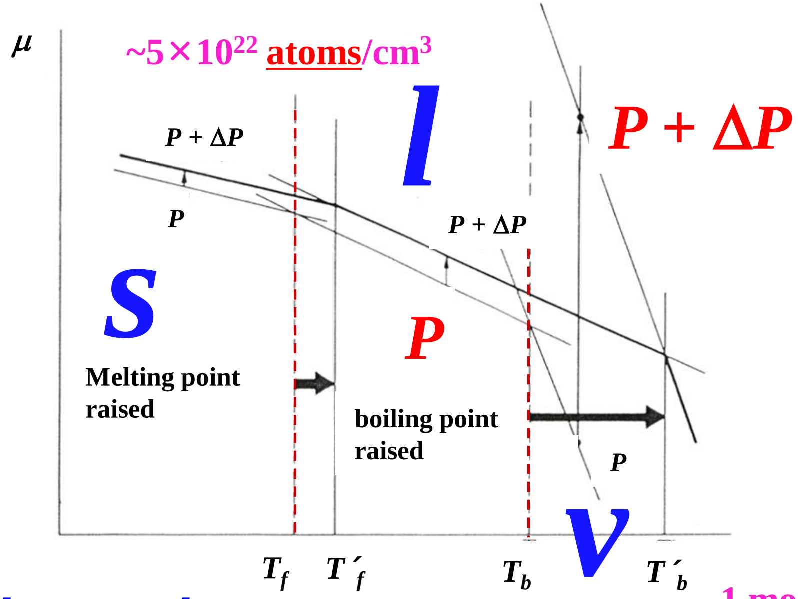
$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$\mu = G_m$$

An increase in pressure raises the chemical potential (because *V* is certainly positive), and increases it much more for gases than either liquids or solids.

The molar volume of **gas** is **~1000 times** larger than that of **liquid or solid**.

An increase in pressure increases the chemical potential of a liquid slightly more than the potential of a solid, resulting in the raising of the freezing point.



~5×10^{22} atoms/cm^3

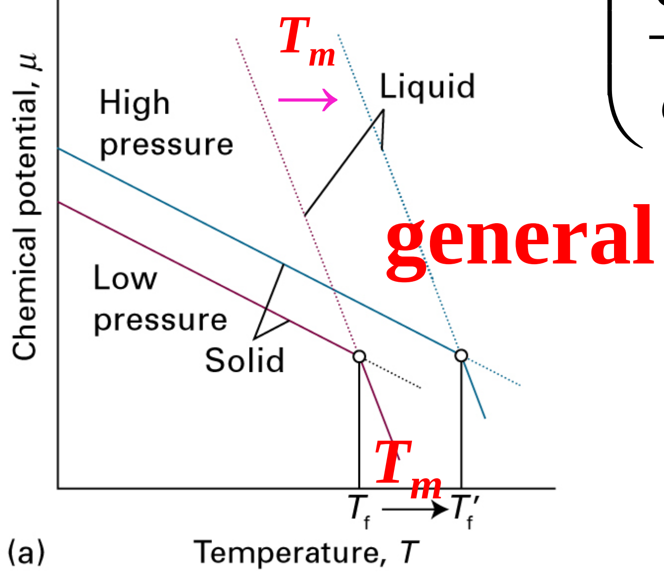
Figure 4B.2

The pressure dependence of the chemical potential, and its effect on the melting and boiling points.

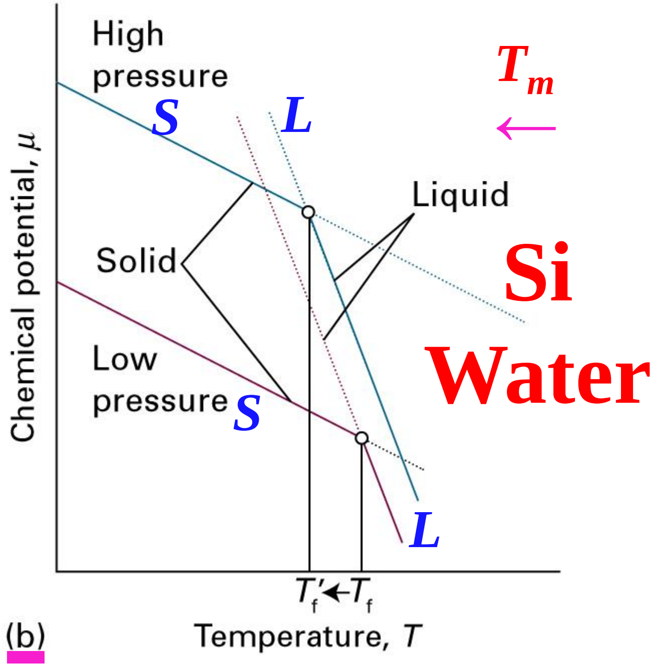
1 mole of gas (6×10^{23} atoms or molecules) in 22.4 liter

Figure 4B.2

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



S - L



The pressure dependence of the chemical potential depends on the molar volume of the phase. In nature, the lines should be curved.

(a) In general, the molar volume of solid is less than that of the liquid, and $\mu(s)$ increases less than $\mu(l)$. As a result, the freezing temperature rises.

(b) The molar volume is greater for the solid than the liquid (as for **Si or water**): $\mu(s)$ increases more strongly than $\mu(l)$. The freezing temperature is lowered.

4B.2. The Location of Phase Boundaries

solid - liquid
liquid - vapor
solid - vapor
α phase - β phase

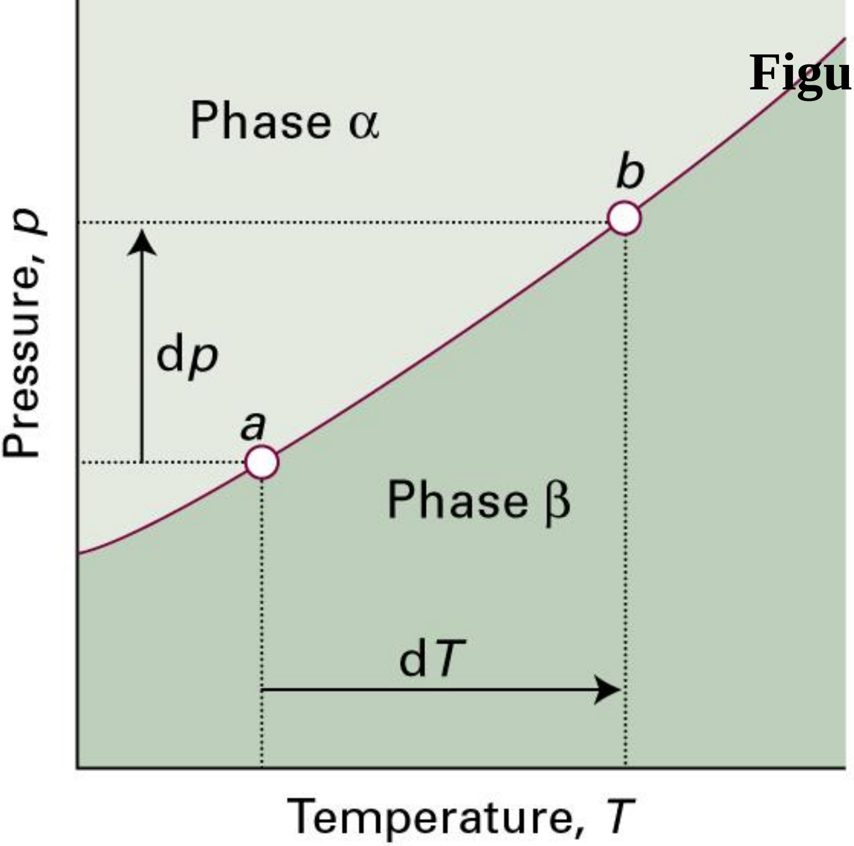


Figure 4B.4

When pressure is applied to a system in which two phases are in equilibrium (at *a*), the equilibrium is disturbed.

It can be restored by changing the temperature, so moving the state of the system to *b*. It follows that there is **a relation between *dp* and *dT*** that ensures that the system remains in equilibrium as either variable is changed.

-Wed/Apr/06/22

Boundary of α Phase – β Phase

4B.2(a). Phase Diagrams

The boundaries between two phases lie at the values of *p* and *T* where the two phases can exist.

$$\text{phase}\ \alpha \ <\text{-}> \text{phase}\ \beta$$

$$\mathbf{G_\alpha = G_\beta \ \ at\ T_{tr}\ \&\ P_{tr}}$$

$$\underline{\mu(\alpha; p, T) = \mu(\beta; p, T)} \qquad (1)$$

$$dG = -SdT + Vdp$$

$$dG_m = d\mu = -S_m dT + V_m dp \qquad (2)$$

Combining Eqs. (1) and (2), we know

$$\underline{-S_m(\alpha)dT + V_m(\alpha)dp = -S_m(\beta)dT + V_m(\beta)dp} \qquad (3)$$

$$\{V_m(\alpha) - V_m(\beta)\}dp = \{S_m(\alpha) - S_m(\beta)\}dT$$

$$\underline{\frac{dp_{tr}}{dT_{tr}} = \frac{\Delta S_m}{\Delta V_m}} \qquad (4)$$

Clapeyron equation
French: [klapɛʁɔ̃]

(4B.5a)

where $\Delta S_m = S_m(\alpha) - S_m(\beta),\ \Delta V_m = V_m(\alpha) - V_m(\beta)$

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\,\Delta V_{tr}}$$

Solid-Liquid Boundary

At the melting point T_f

$$\Delta G_m = \Delta H_{melt,m} - T_f \Delta S_m = 0$$

$G_s = G_l$ at T_m

The molar entropy change of melting

$$\Delta S_m = \frac{\Delta H_{melt,m}}{T_f}$$

From eq (4)

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\frac{dp}{dT} = \frac{\Delta H_{melt,m}}{T_f \Delta V_m} \qquad (5) \qquad \textbf{(4B.6)}$$

melting = fusion

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\ \Delta V_{tr}}$$

On integrating eq (5), the equation of the solid-liquid equilibrium curve

$$p = p^* + \frac{\Delta H_{melt,m}}{\Delta V_m} \ln \frac{T}{T^*} \qquad (6)$$

(assuming latent heat independent of *P* and *T*)

where *p** and *T** are the pressure and temperature on some point of the equilibrium line.

When *T* is close to *T**, the logarithm can be approximated using

$$\ln\left(\frac{T}{T^*}\right) = \ln\left(1 + \frac{T - T^*}{T^*}\right) \approx \frac{T - T^*}{T^*}$$

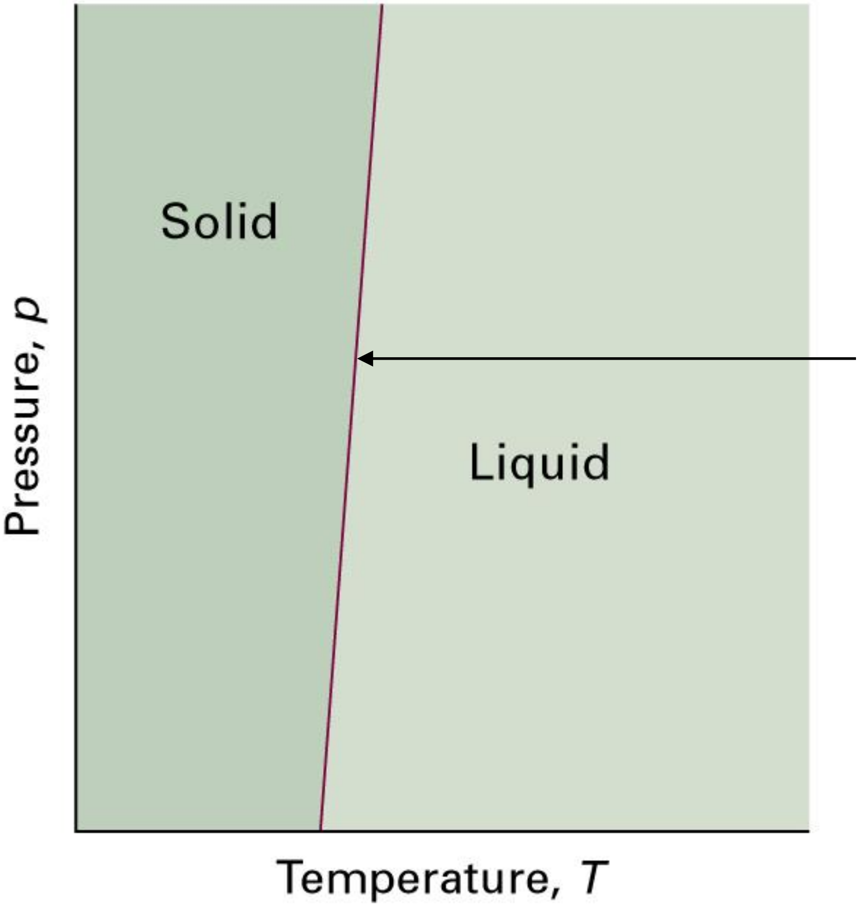
$$\therefore\ p = p^* + \left(\frac{\Delta H_{melt,m}}{T^* \Delta V_m}\right)(T - T^*)$$

(4B.8)

which is linear in *T*.

$$T^* + \Delta T = T \qquad p^* + \Delta p = p$$

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\,\Delta V_{tr}}$$



$$p = p^* + \left(\frac{\Delta H_{melt,m}}{T^*\Delta V_m}\right)(T - T^*)$$

Figure 4B.5
A typical solid-liquid phase boundary slopes steeply upwards.
This slope implies that, as the pressure is raised, the melting temperature rises.
Most substances behave in this way.

Note that water freezes 0°C at 1 *atm*.

Example:

What is the freezing point of water under a pressure of 1500 *atm*?

$$\Delta H_{melt,m} = 6.01 kJ/mol$$

$$\Delta V_{melt,m} = -1.7 cm^3/mol$$

~0.5 eV/atom in Si

(assuming independent of *P* and *T*)

Solution:

$$T = T^* \exp\left\{\left(p - p^*\right)\Delta V_{melt,m} / \Delta H_{melt,m}\right\} \leftarrow p = p^* + \frac{\Delta H_{melt,m}}{\Delta V_m} \ln\frac{T}{T^*}$$

$$= 273.15K \exp\left\{\frac{(1500-1)\left(1.013\times10^5 Nm^{-2}\right)\left(-1.7cm^3/mol\right)}{6.01kJ/mol}\right\}$$

$$= 273.15K \exp(-0.043)$$

$$= 261.7K$$

$$\Delta T = T - T^* = \underline{-11.5^0 C}$$

4B.2(c). The Liquid-Gas Boundary

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\,\Delta V_{tr}}$$

$\Delta H_{vap,m}$: the molar enthalpy of vaporization

$\Delta V_{vap,m}$: the molar volume change on vaporization

$$\frac{dp}{dT} = \frac{\Delta H_{vap,m}}{T\Delta V_{vap,m}}$$ the Clapeyron equation $$\frac{dp}{dT} = \frac{\Delta H_{melt,m}}{T_{tr}\Delta V_{melt,m}}$$

$\Delta H_{vap,m} > 0, \Delta V_{vap,m}$

$\therefore \dfrac{dp}{dT}$ is much smaller than in the case of solid-liquid equilibrium.

The slope depends on $\Delta V_{vap,m}$, and the volume of the gas is sensitive to P.
Increasing pressure decreases $V(g)$ and therefore $\Delta V_{vap,m}$ also.
The slope $\left(\dfrac{dp}{dT}\right)$ increases as p increases, and this is why the line drawn in Figure 4B.7 curls upwards.

Assuming that the gas behaves ideally, $V_m(g)$ may be replaced by

$$\frac{dp}{dT}=\frac{\Delta H_{vap,m}}{T\left(\frac{RT}{p}\right)}=\frac{p\Delta H_{vap,m}}{RT^2} \qquad \Delta V_{vap,m}=V_m(g)-V_m(l)\approx V_m(g)$$

On rewriting,

$$\frac{d(\ln p)}{dT}=\frac{\Delta H_{vap,m}}{RT^2} \quad \text{Clausius - Clapeyron equation} \quad (7)$$

(4B.10)

Assuming that $\Delta H_{vap,m}$ does not depend on the temperature,

$$p=p^{*}\exp\left\{\frac{-\Delta H_{vap,m}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right\}$$

(4B.11)

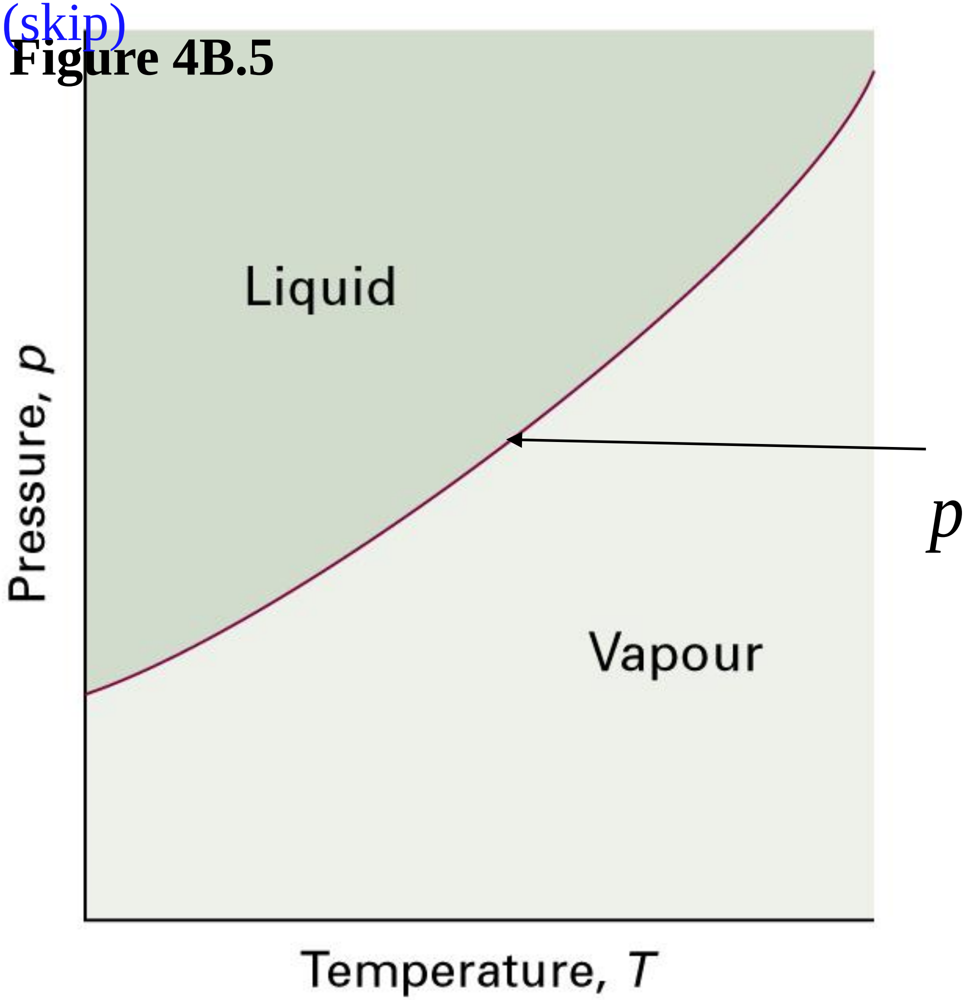
Ideal Gas +
Negligible Volume of Liquid

where p^* is the pressure at some temperature T^*.

(skip)

(skip)

Figure 4B.5



$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\ \Delta V_{tr}}$$

$$p = p^{*} \exp\left\{\frac{-\Delta H_{vap,m}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right\}$$

Ideal Gas +
Negligible Volume of Liquid

A typical liquid-vapor phase boundary.

The boundary can be regarded as a plot of the vapor pressure against *T*.

The phase boundary terminates at the critical point (not shown).

4B.2(c). Solid-Vapor Boundary

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta S_{tr}}{\Delta V_{tr}} = \frac{\Delta H_{tr}}{T_{tr}\,\Delta V_{tr}}$$

$\Delta H_{sub,m}$: the molar enthalpy of sublimation

Similarly,

$$p = p^{*}\exp\left\{\frac{-\Delta H_{sub,m}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right\} \qquad p = p^{*}\exp\left\{\frac{-\Delta H_{vap,m}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right\}$$

usu. $\Delta H_{sub,m} > \Delta H_{vap,m}$

The slope $\dfrac{dp}{dT}$ is steeper for sublimation than for vaporization. (See Fig. 4B.8)

The Solid-Liquid-Gas Equilibrium

Triple Point: A point where solid, liquid, and gas can all coexist in equilibrium. It is given by the values of p and T for which all three chemical potentials are equal.

4B.3. More Remarks about Phase Transitions

At the transition point,

ΔS at T_{tr}

$$\Delta H_m = T\Delta S_m = -T\left(\frac{\partial \Delta\mu}{\partial T}\right)_p = -T\left\{\left(\frac{\partial \mu(\beta)}{\partial T}\right)_p - \left(\frac{\partial \mu(\alpha)}{\partial T}\right)_p\right\} \neq 0$$

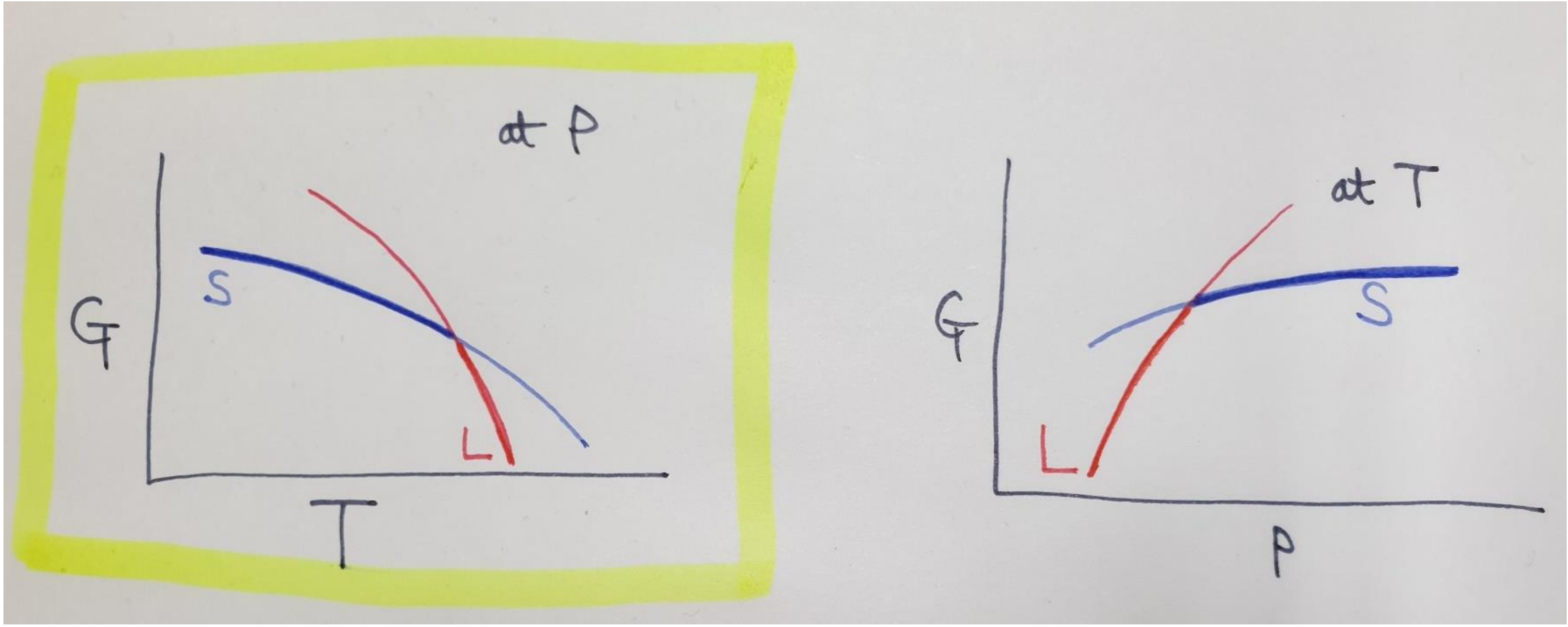
ΔV at P_{tr}

$$\Delta V_m = \left(\frac{\partial \Delta\mu}{\partial p}\right)_T = \left(\frac{\partial \mu(\beta)}{\partial p}\right)_T - \left(\frac{\partial \mu(\alpha)}{\partial p}\right)_T \neq 0$$

Since both ΔV_m and ΔH_m are non-zero, it follows that $\left(\frac{\partial \mu}{\partial p}\right)_T$ and $\left(\frac{\partial \mu}{\partial T}\right)_p$ can be different on either side of the transition. In other words, the **derivatives of Gibbs free energy can be discontinuous**. This is the basis of the term ***the First-Order Phase Transition***.

The case in which the first derivative of *G* is continuous, but the second derivative is discontinuous.

→ ***the Second-Order Phase Transition***.



True,
all the time.

In general,
but not all the time.

Second-Order Phase Transition

A continuous slope of μ implies that the **entropy and volume** (and hence the enthalpy) do not change at the transition.

The heat capacity is discontinuous at the transition but does not become infinite.

The type of 2^{nd}-order transition may include:

ΔS at T_{tr}

ΔV at P_{tr}

- **Order-Disorder Transition**
- **Ferromagnetic Transition**
- **Ferroelectric Transition**
- **Fluid-Superfluid Transition**

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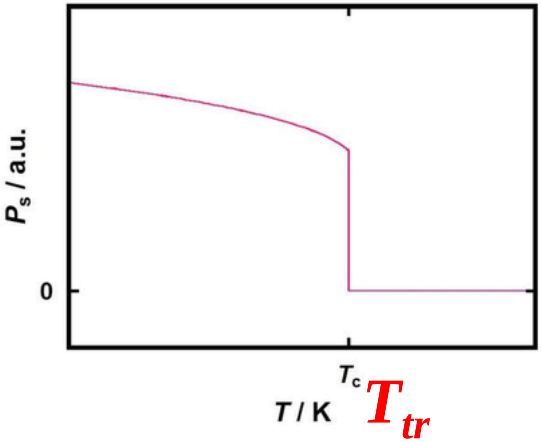

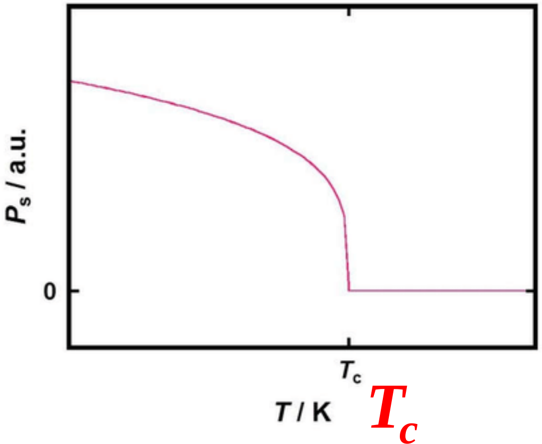

$$\Delta H_m = T\Delta S_m = -T\left(\frac{\partial \Delta\mu}{\partial T}\right)_p = -T\left\{\left(\frac{\partial \mu(\beta)}{\partial T}\right)_p - \left(\frac{\partial \mu(\alpha)}{\partial T}\right)_p\right\} \neq 0$$

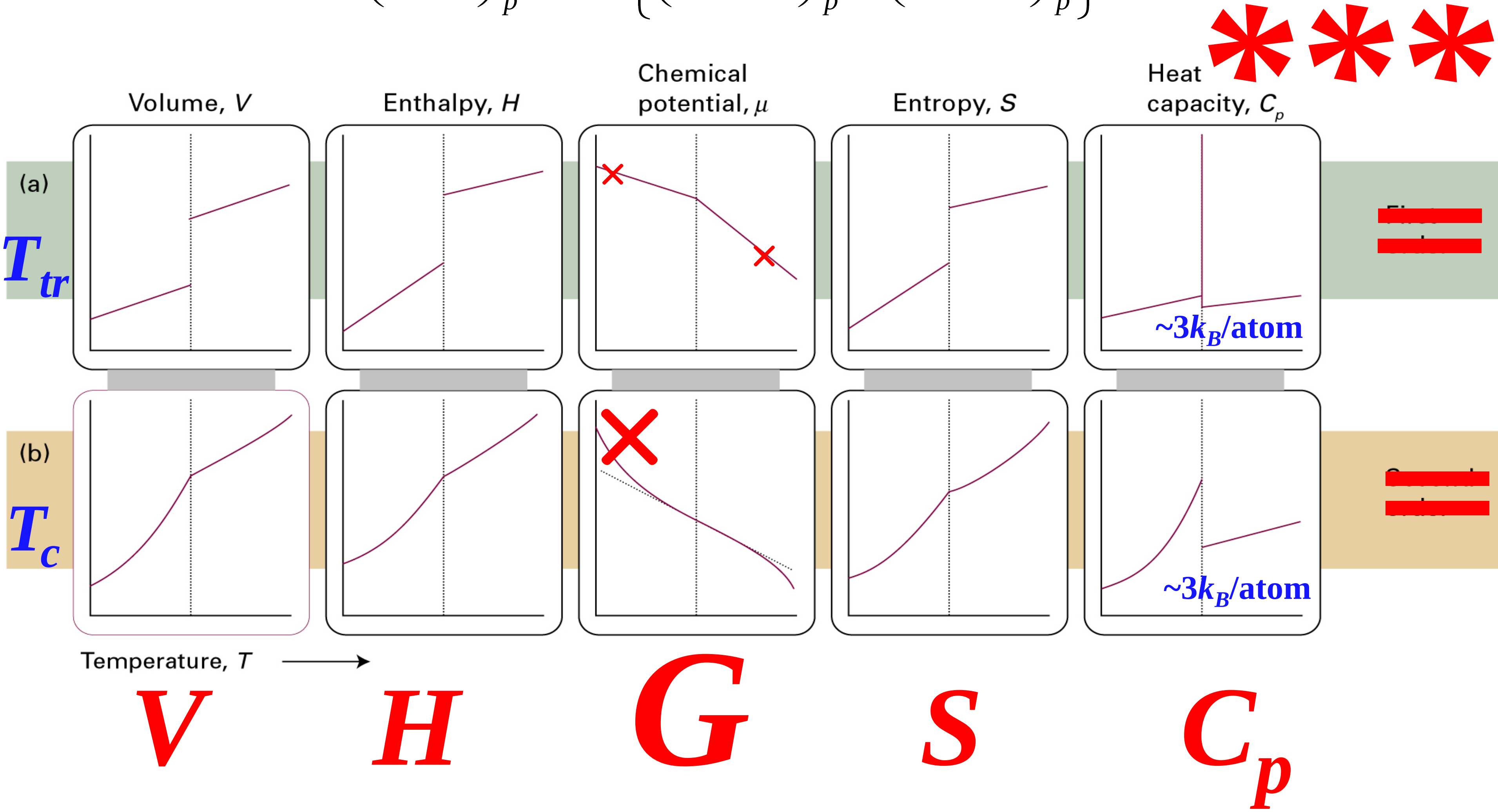

Figure 4B.9
(a) first-order and (b) second-order phase transitions.

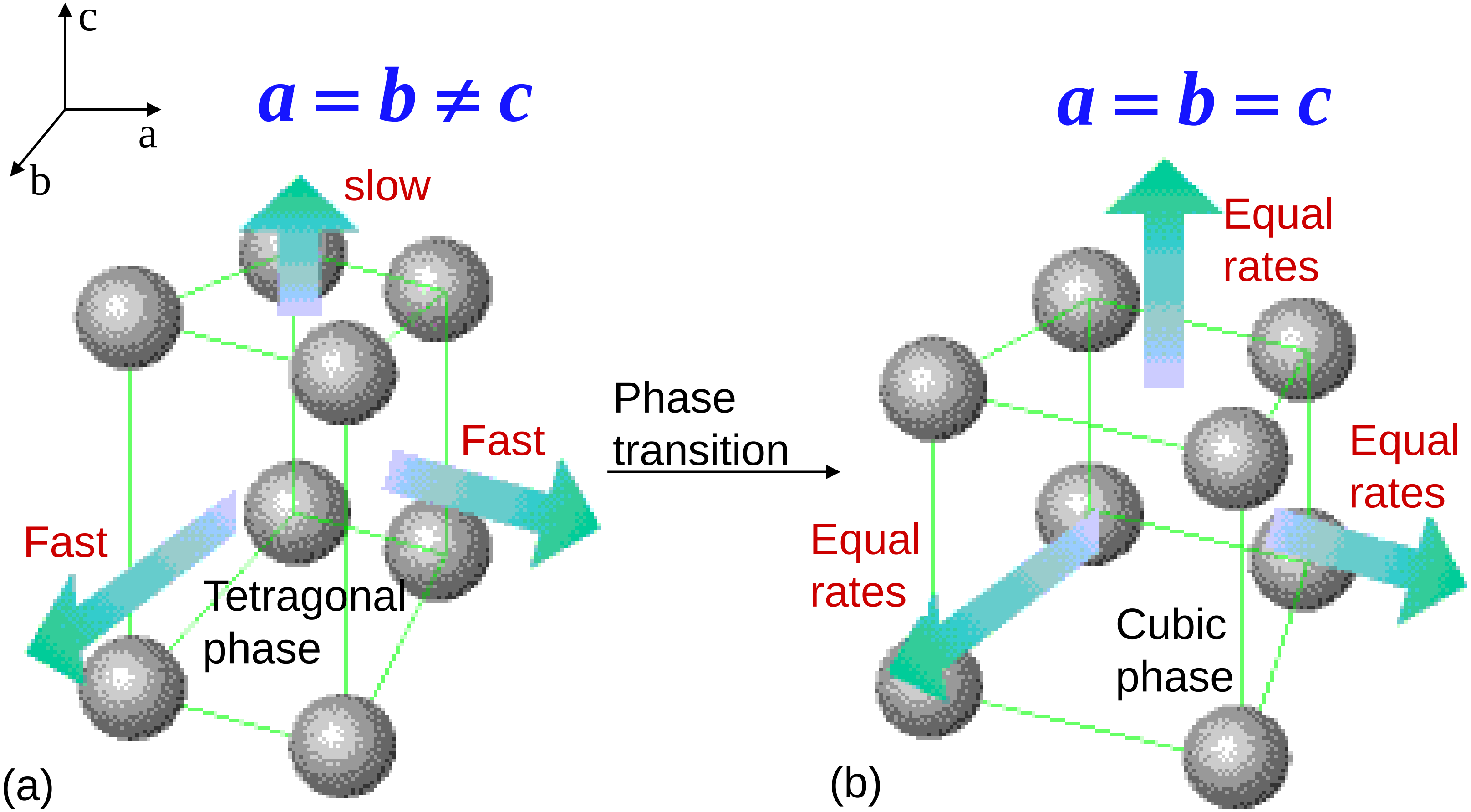

Fig. 4B.11 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised.

There is no major rearrangement of atoms at the transition temperature, and hence the enthalpy of transition may become zero.

Example: Perovskite Semiconductor

Formamidinium
Methylammonium

$[Cs_{0.05}[\{CH(NH_2)_2\}_{0.83}\{CH_3NH_3\}_{0.17}]_{0.95}]Pb(I_{0.83}Br_{0.17})_3 = ABX_3$

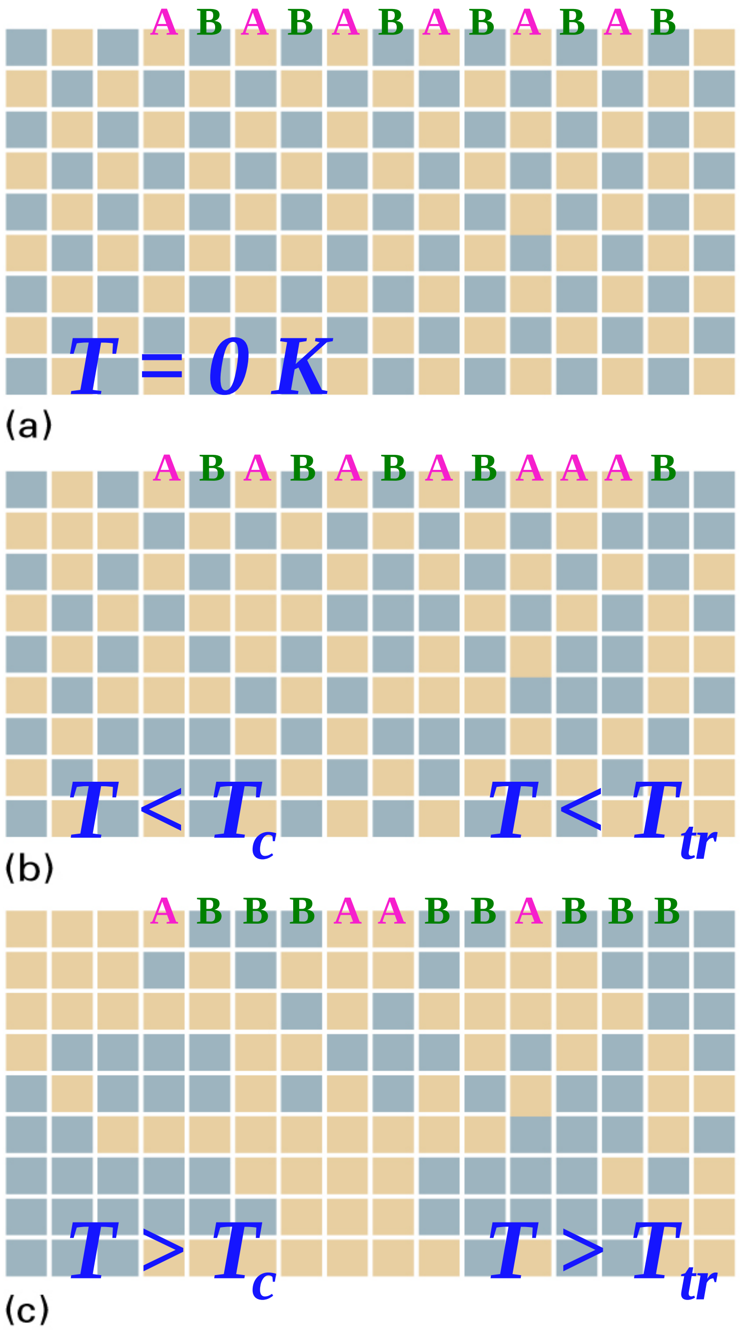

Figure 4B.12

Order-Disorder Transition

(a) At $T = 0$, there is perfect order, with different kinds of atoms occupying alternate sites.

(b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives.

(c) At and above the transition temperature, the islands occur at random throughout the sample.

***A* and *B* atoms like each other, compared to the *A*-*A* or *B*-*B* atoms.**

Problems from Chap. 4

4A.4

4A.2(b)

4B.2 4B.4

4B.5(b)

4B.6 4B.12