

## Physical transformations of pure substances

Boiling, freezing, and the conversion of graphite to diamond – examples of **phase transitions** – changes of phase without change of chemical composition. In this chapter we describe such processes thermodynamically, using the tendency of systems at constant temperature and pressure to minimize their Gibbs energies.

### Phase diagrams: The stabilities of phases

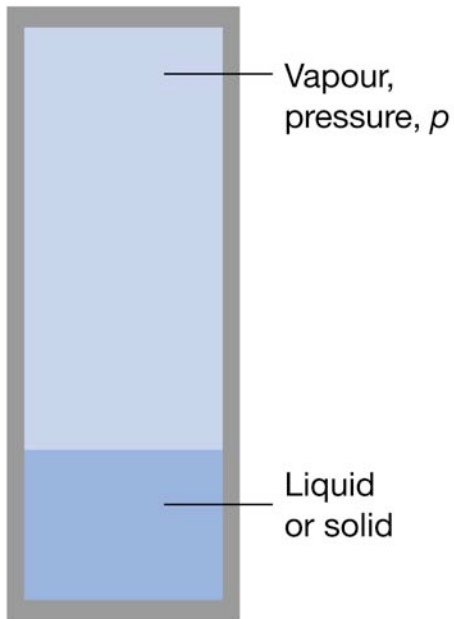
A **phase** of a substance – uniform throughout in chemical composition and physical state: solid, liquid, and gas phases of a substance; its various solid phases (the white and black allotropes of phosphorus, graphite and diamond, monoclinic and orthorhombic sulfur, etc.)

A **phase transition** – the spontaneous conversion of one phase to another occurring at a characteristic temperature at a given pressure. The **transition temperature**,  $T_{\text{trs}}$  – the temperature at which two phases are in equilibrium at the prevailing pressure. We must distinguish between the thermodynamic description of a phase transition and the rate at which the transition occurs. A transition, which is spontaneous according to thermodynamics, may occur too slowly to be significant in practice. Example: graphite and diamond – at normal  $T$  and  $p$  the molar Gibbs energy of graphite is lower than that of diamond – there is a thermodynamic tendency for diamond to change into graphite. However, for the transition to occur, the C atoms must change their locations, which a very slow process in a solid, unless  $T$  is very high. The rate to reach equilibrium is a kinetic problem outside the range of thermodynamics. In gases and liquids, the molecules are mobile and phase transitions occur rapidly, but in solids thermodynamic instability may be frozen in. Thermodynamically unstable phases that persist because the transition is kinetically hindered – metastable phases.

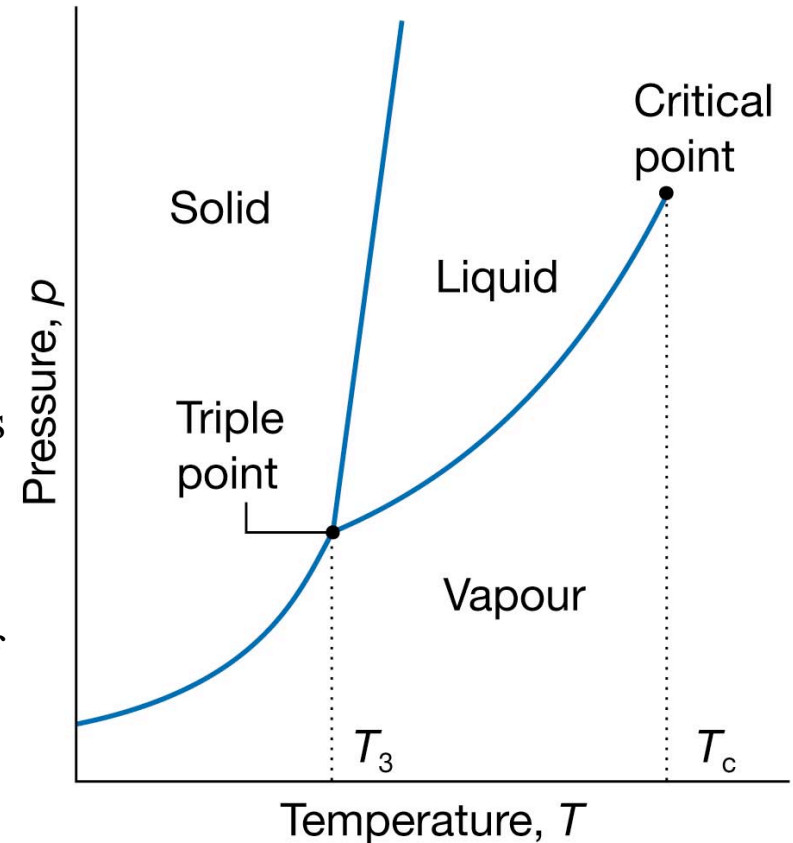
## Phase boundaries

The **phase diagram** of a substance – a map that shows the regions of temperature and pressure at which its various phases are thermodynamically most stable.

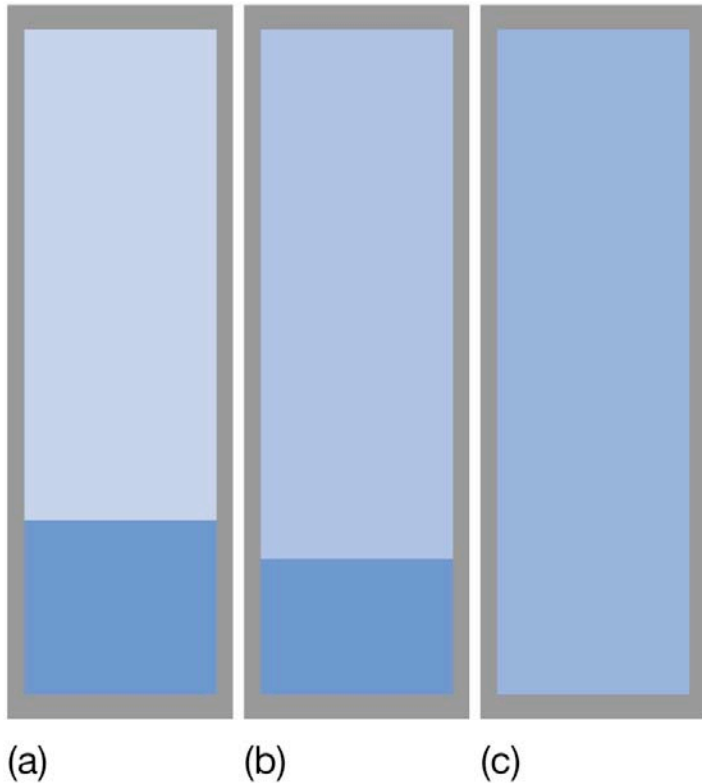
The boundaries between regions (**phase boundaries**) show the values of  $p$  and  $T$  at which the two neighboring phases are in equilibrium.



The pressure of vapor in equilibrium with its liquid - **vapor pressure**. The liquid-vapor phase boundary shows the variation of the vapor pressure with temperature. The solid-vapor phase boundary - shows the variation of the **sublimation vapor pressure** with temperature.



When a liquid is heated in an open vessel, the liquid vaporizes from its surface. At a certain  $T$ , its vapor pressure becomes equal to the external pressure - vaporization can occur throughout the bulk of the liquid and the vapor can expand freely into the surroundings. Free vaporization through the liquid - **boiling**. The temperature at which the vapor pressure is equal to the external pressure - **boiling temperature** at that pressure.  $p_{\text{ex}} = 1 \text{ atm}$  - **normal boiling point**,  $T_b$  ( $100^\circ\text{C}$  for water).  $p_{\text{ex}} = 1 \text{ bar}$  - **standard boiling point** ( $99.6^\circ\text{C}$  for water).



Boiling does not occur when a liquid is heated in a closed vessel. The vapor pressure and the density of the vapor rise continuously as  $T$  is raised. Meanwhile, the density of the liquid decreases as a result of its expansion. At a certain stage, the vapor density becomes equal to that of the remaining liquid - the surface between the two phases disappears. The temperature at which the surface disappears - the **critical temperature**,  $T_c$ . The vapor pressure at  $T_c$  - **critical pressure**,  $p_c$ . A single uniform phase at and above the critical temperature - a **supercritical fluid**. It fills the container and an interface no longer exists. Above the critical temperature, the liquid phase of a substance does not exist.

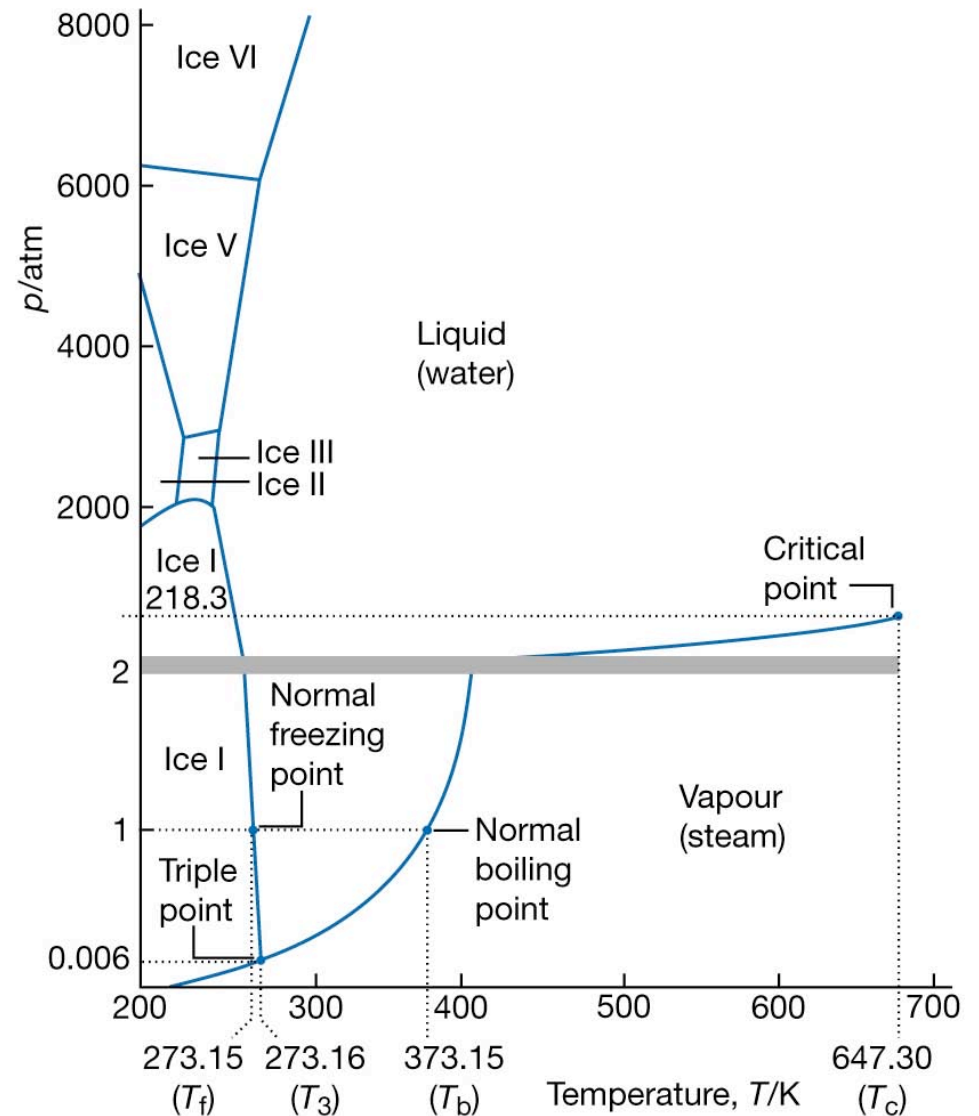
The **melting temperature** - the temperature at which (under a specified  $p$ ) the liquid and solid phases coexist in equilibrium. The melting temperature of a substance is the same as its **freezing temperature**. The freezing temperature at  $p = 1$  atm - the **normal freezing point (normal melting point)**,  $T_f$ ; at  $p = 1$  bar - the **standard freezing point**.

There is a set of conditions ( $p, T$ ) under which three different phases of a substance (solid, liquid, and vapor) all simultaneously coexist in equilibrium - the **triple point** - a point at which the three phase boundaries meet. The temperature at the triple point -  $T_3$ . The triple point of a pure substance is unique and outside of our control: occurs at a single definite pressure and temperature characteristic of the substance. The triple point of water: 273.16 K, 611 Pa (6.11 mbar, 4.58 Torr).

The liquid-vapor phase boundary shows how the vapor pressure of liquid water varies with temperature. It can be used to decide how the boiling temperature varies with changing the external pressure. The solid-liquid boundary shows how the melting temperature varies with pressure. This line shows a negative slope up to 2 kbar - the melting temperature falls as the pressure is raised. The reason - the decrease of volume on melting - it is more favorable for the solid to transform into the liquid as  $p$  is raised. The decrease in volume - the result of the very open molecular structure of ice: the  $H_2O$  molecules are held apart (or together) by the hydrogen bonds, but the structure partially collapses on melting and the liquid is denser than the solid.

Water has many different solid phases other than ordinary ice (ice I). They differ in the arrangement of the water molecules: under the influence of very high pressures, hydrogen bonds buckle and the  $H_2O$  molecules adopt different arrangements. These **polymorphs** of ice may be responsible for the advance of glaciers – ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.

## Three typical phase diagrams Water



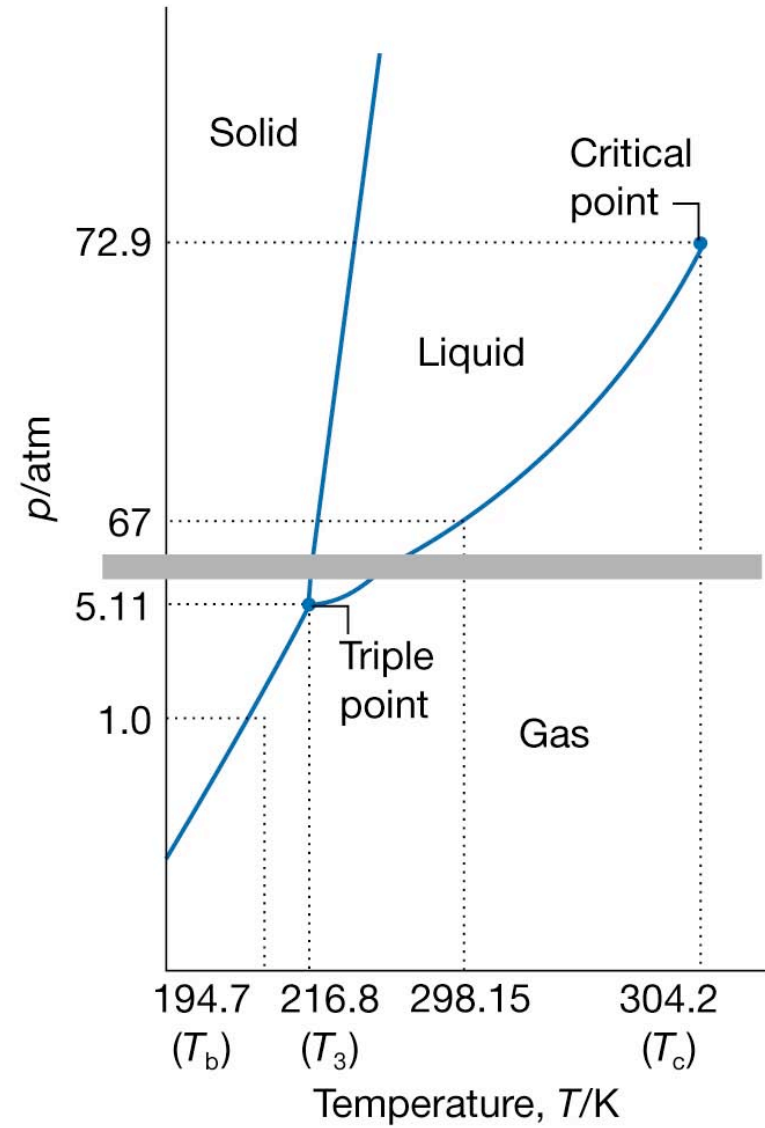
Some of ice polymorphs melt at high  $T$ :  $100^\circ\text{C}$  for ice VII (exists only above 25 kbar).  
Five more triple points occur in the diagram.

## The phase diagram for carbon dioxide

The slope of the solid-liquid boundary is positive – typical for almost all substances. The slope indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased.

The triple point (217 K, 5.11 bar) lies well above ordinary atmospheric pressure – liquid carbon dioxide does not exist at normal atmospheric pressures whatever the temperature, and the solid sublimates when left in the open ('dry ice'). To obtain liquid carbon dioxide, it is necessary to exert a pressure of at least 5.11 bar.

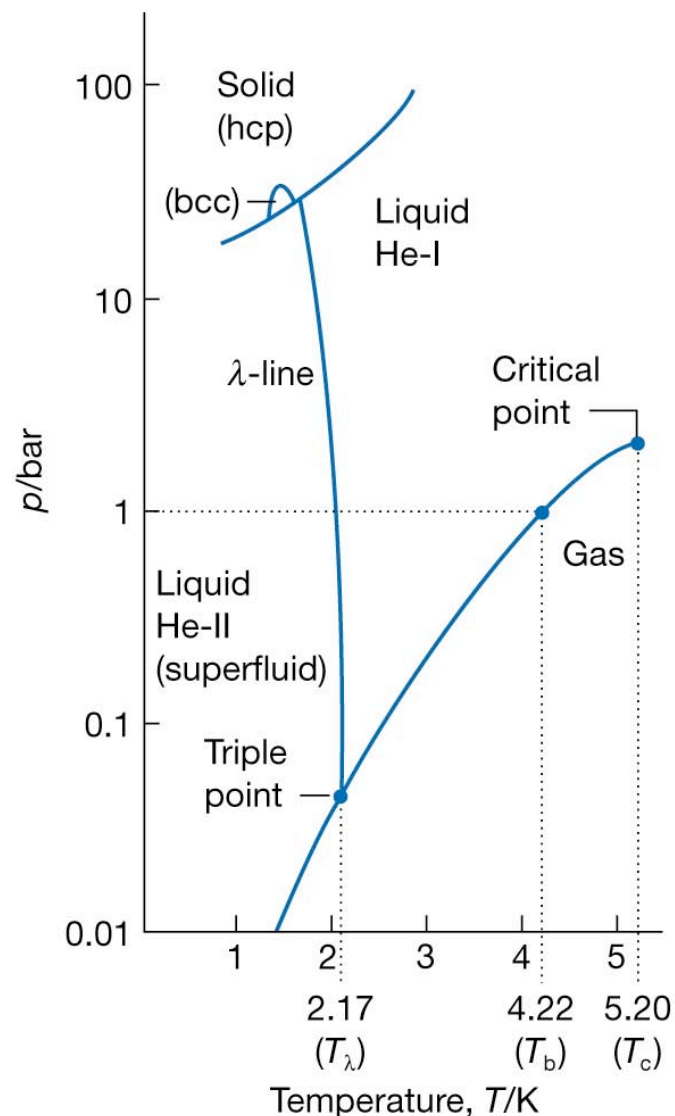
Cylinders of carbon dioxide generally contain the liquid or compressed gas. If both gas and liquid are present inside the cylinder, then at 25°C the pressure must be about 67 atm. When the gas squirts through the throttle it cools by the Joule-Thomson effect so, when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.



## The phase diagram of helium

Helium behaves unusually at low temperatures. The solid and gas phases of helium are never in equilibrium however low the temperature: the atoms are so light that they vibrate with a large-amplitude motion even at very low temperatures and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure. A second unique feature of helium is that pure helium-4 has two liquid phases. The phase He-I behaves like a normal liquid, while He-II is a **superfluid**; it is so called because it flows without viscosity. Helium is the only known substance with a liquid-liquid boundary in its phase diagram.

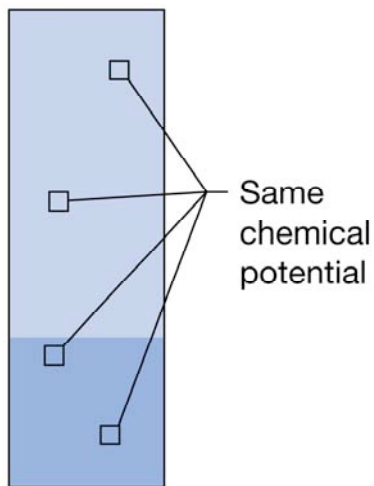
The phase diagram of helium-3 differs from the phase diagram of helium-4, but it also has a superfluid phase. Helium-3 is unusual - the entropy of the liquid is lower than that of the solid - melting is exothermic.



## Phase stability and phase transitions

Our consideration is based on the Gibbs energy of a substance, in particular, its *molar* Gibbs energy. The Gibbs energy of a sample of substance,  $G$ , is equal to  $nG_m$ , where  $n$  is the amount of substance in the sample and  $G_m$  is its molar Gibbs energy. **Chemical potential**,  $\mu$ : for a one-component system, ‘molar Gibbs energy’ and ‘chemical potential’ are synonyms,  $\mu = G_m$ . Later we shall see that chemical potential has a broader significance and a broader definition – it is a measure of the potential that a substance has for bringing about physical or chemical change in a system.

### The thermodynamic criterion of equilibrium



*At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.*

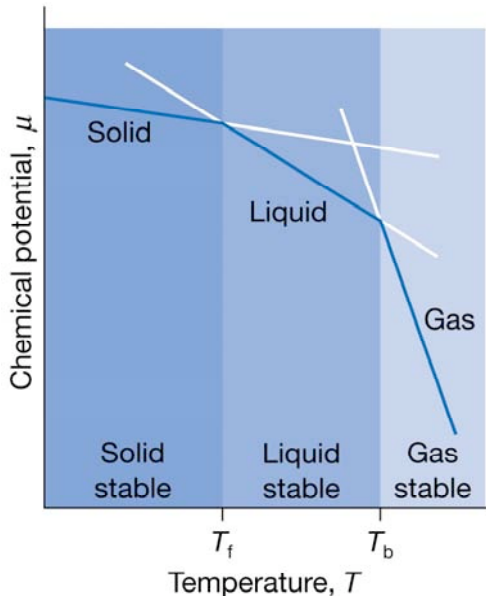
Consider a system where the chemical potential of a substance is  $\mu_1$  at one location and  $\mu_2$  at another location. The locations may be in the same or in different phases. When an amount  $dn$  of the substance is transferred from one location to the other, the Gibbs energy of the system changes by  $-\mu_1 dn$  when material is removed from location 1, and by  $+\mu_2 dn$  when that material is added to location 2. The overall change is

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

If  $\mu_1 > \mu_2$ , the transfer is accompanied by a decrease in  $G$  and has a spontaneous tendency to occur. If  $\mu_1 = \mu_2$ ,  $dG = 0$  and only then the system is in equilibrium. The transition temperature,  $T_{\text{trs}}$  – the temperature at which the chemical potentials of two phases are equal.

### The dependence of stability on the conditions

At low temperatures, the solid state of a substance has the lowest chemical potential and (if the pressure is not too low) is usually the most stable at low temperatures. However, the chemical potentials of phases change with temperature in different ways, and as  $T$  is raised, the chemical potential of another phase (another solid phase, a liquid, or a gas) will become below that of the solid. Then, a phase transition occurs, if it is kinetically feasible.



### The temperature dependence of phase stability

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \qquad \text{As the temperature is raised,}$$

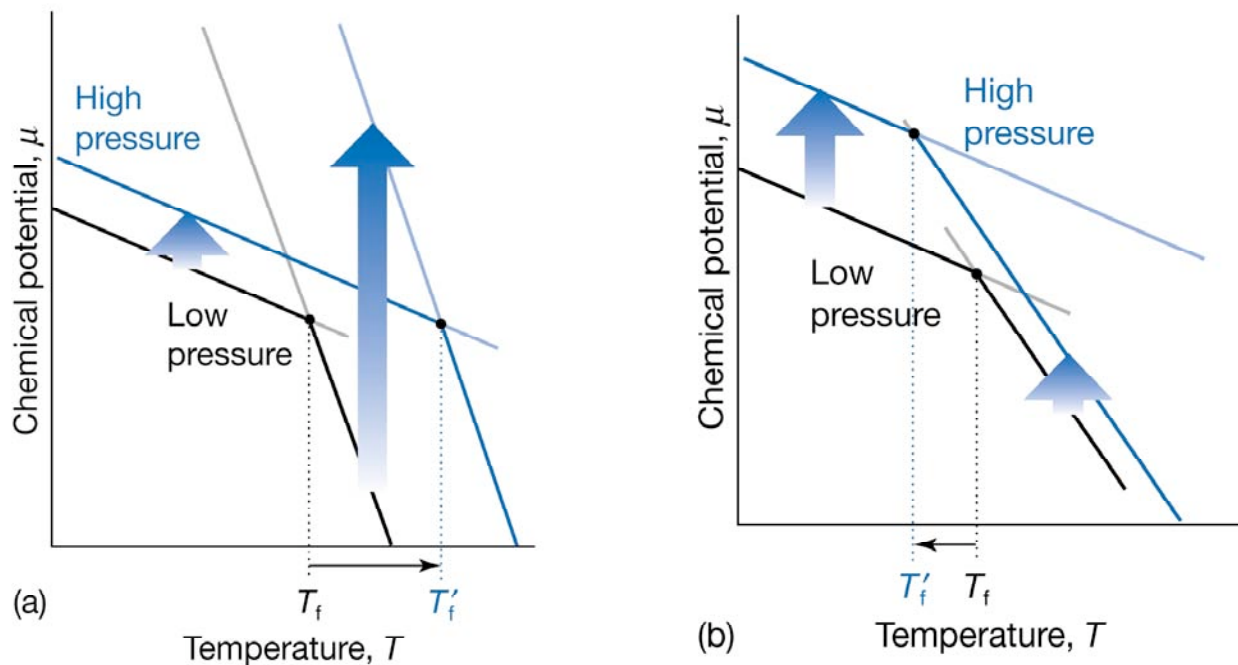
the chemical potential of a pure substance decreases:  $S_m > 0$  for all substances is negative, the slope of a plot of  $\mu$  against  $T$  is negative. The slope of a plot of  $\mu$  against  $T$  is steeper for gases than for liquids:  $S_m(\text{g}) > S_m(\text{l})$ . Also, the slope is steeper for a liquid than for the solid:  $S_m(\text{l}) > S_m(\text{s})$ , as a liquid has a greater disorder. Because of the steep negative slope,  $\mu(\text{l})$  falls below  $\mu(\text{s})$  when the temperature is high enough – the liquid becomes the stable phase and the solid melts.

The chemical potential of the gas phase plunges steeply downwards as  $T$  is raised and  $\mu(\text{g})$  becomes lower than  $\mu(\text{l})$ . Then the gas is the stable phase and the liquid vaporizes. A phase transition is caused by the change of the relative values of the chemical potentials of the phases. The easiest way to modify  $\mu$  - by changing the temperature of the sample.



## The response of melting to applied pressure

Most substances melt at a higher temperature when subjected to pressure – the pressure is preventing the formation of the less dense liquid phase. Exception – water – the liquid is denser than the solid and water freezes at a lower temperature when it is under pressure.



$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$  - the slope of a plot of  $\mu$  against pressure is  $V_m$ . An increase in pressure raises the chemical potential of any pure substance ( $V_m > 0$ ). In most cases  $V_m(l) > V_m(s)$  and an increase in pressure increases the chemical potential of the liquid more than that of the solid – then, the effect of pressure is to raise the melting temperature slightly. For water,  $V_m(l) < V_m(s)$ , and an increase in

pressure increases the chemical potential of the solid more than that of the liquid – the melting temperature is lowered slightly.

*Example 1. Assessing the effect of pressure on the chemical potential.*

Calculate the effect on the chemical potential of ice and water of increasing pressure from 1.00 bar to 2.00 bar at 0°C. The density of ice is 0.917 g cm<sup>-3</sup> and that of liquid water is 0.999 g cm<sup>-3</sup> under these conditions.

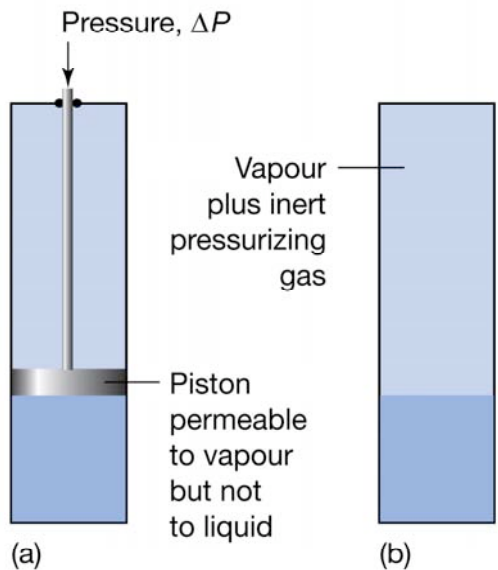
$$\Delta\mu = V_m\Delta p \quad \rho = M/V_m \quad V_m = M/\rho \quad \Delta\mu = M\Delta p/\rho$$

$$\Delta\mu(\text{ice}) = (1.802 \times 10^2 \text{ kg mol}^{-1}) \times (1.0 \times 10^5 \text{ Pa}) / (917 \text{ kg m}^{-3}) = +1.97 \text{ J mol}^{-1}$$

$$\Delta\mu(\text{water}) = (1.802 \times 10^2 \text{ kg mol}^{-1}) \times (1.0 \times 10^5 \text{ Pa}) / (999 \text{ kg m}^{-3}) = +1.80 \text{ J mol}^{-1}$$

The chemical potential of ice rises more sharply than that of water. If they are initially at equilibrium at 1 bar, there will be a tendency for the ice to melt at 2 bar.

### The effect of applied pressure on vapor pressure



When pressure is applied to a condensed phase, its vapor pressure rises – molecules are squeezed out of the phase and escape as a gas. Pressure can be applied on the condensed phases mechanically (a) or by an introduction of an inert gas (b). In case (b) the vapor pressure is the partial pressure of the vapor in equilibrium with the condensed phase – the **partial vapor pressure** of the substance.

$$p = p^* e^{V_m\Delta P/RT}$$

$p^*$  - the vapor pressure of the liquid in the absence of an additional pressure;  $p$  - the vapor pressure of the liquid,  $\Delta P$  – the applied pressure.

$$\text{for } x \ll 1, \quad p = p^* e^{V_m\Delta P/RT} \quad p \approx p^* \left(1 + \frac{V_m\Delta P}{RT}\right) \quad \frac{p - p^*}{p^*} \approx \frac{V_m\Delta P}{RT}$$

$$e^x = 1 + x + \frac{1}{2}x^2 + \dots \approx 1 + x$$

**Proof:** we calculate the vapor pressure of a pressurized liquid based upon the fact that  $\mu(l) = \mu(g)$ . For any change that preserves equilibrium:  $d\mu(l) = d\mu(g)$ . When the pressure  $P$  of the liquid is increased by  $dP$ ,  $d\mu(l) = V_m(l)dP$   $d\mu(g) = V_m(g)dp$   
 $dp$  – the change in the vapor pressure we are trying to find.

$$V_m(g) = \frac{RT}{p} \quad d\mu(g) = \frac{RTdp}{p} \quad \frac{RTdp}{p} = V_m(l)dP$$

We can integrate the last expression once we know the limits of integration. When there is no additional pressure acting on the liquid,  $P$  (the pressure experienced by the liquid) is equal to the normal vapor pressure  $p^*$ :  $P = p^*$  and  $p = p^*$ . When there is an additional pressure  $\Delta P$  on the liquid,  $P = p + \Delta P$ , the vapor pressure is  $p$ . The effect of pressure on the vapor pressure is so small that it is a good approximation to replace  $p$  in  $p + \Delta P$  by  $p^*$  itself and to set the upper limit of integration to  $p^* + \Delta P$ .

$$RT \int_{p^*}^p \frac{dp}{p} = \int_{p^*}^{p^* + \Delta P} V_m(l)dP \quad RT \ln \frac{P}{p^*} = V_m(l)\Delta P$$

(Because we can assume that  $V_m(l)$  is the same throughout the small range of pressures involved).

$$\text{For water, } \rho = 0.997 \text{ g cm}^{-3} \text{ at } 25^\circ\text{C} \quad V_m = 18.1 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{At } \Delta P = 10 \text{ bar, } V_m\Delta P/RT = (1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) \times (1.0 \times 10^6 \text{ Pa}) / \{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})\} = 7.3 \times 10^{-3}$$

Because  $V_m\Delta P/RT \ll 1$ , we can use  $\frac{p - p^*}{p^*} \approx \frac{V_m\Delta P}{RT}$ :  $(p - p^*)/p^* = 7.3 \times 10^{-3}$  – an increase of 0.73%.

## The location of phase boundaries

Thermodynamics provides us with a way of predicting the location of phase boundaries. Suppose two phases are in equilibrium at a given pressure and temperature. If we change the pressure, we must adjust the temperature to a different value to ensure the two phases remain in equilibrium – there must be a relation between the change in pressure and the change in temperature, so that the two phases remain in equilibrium. Where two phases are

in equilibrium:  $\mu_\alpha(p, T) = \mu_\beta(p, T)$

Let  $p$  and  $T$  to be changed infinitesimally, but in such a way that the two phases  $\alpha$  and  $\beta$  remain in equilibrium. The chemical potentials of the phases are initially equal and they remain equal when the conditions are changed to another point of the phase boundary:

$$d\mu_\alpha = d\mu_\beta$$

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

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

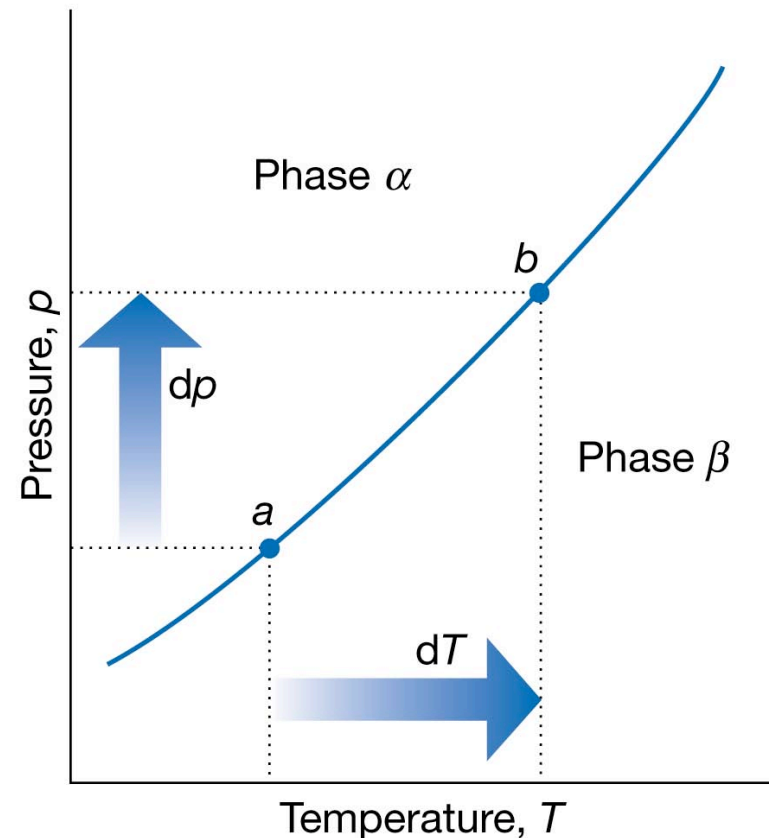
$$(V_{\beta,m} - V_{\alpha,m}) dp = (S_{\beta,m} - S_{\alpha,m}) dT$$

$$\Delta_{\text{trs}} S = S_{\beta,m} - S_{\alpha,m} \quad \Delta_{\text{trs}} V = V_{\beta,m} - V_{\alpha,m}$$

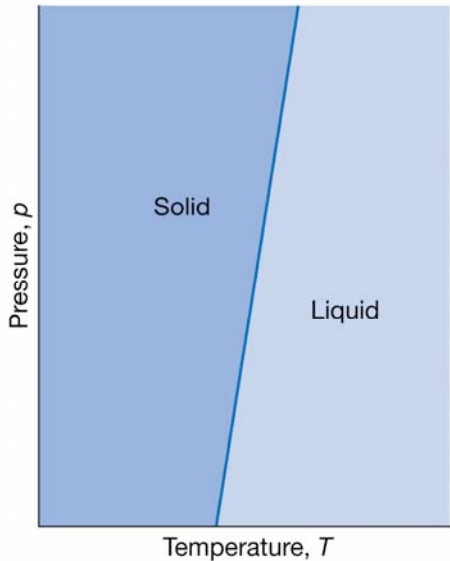
$$\Delta_{\text{trs}} S \times dT = \Delta_{\text{trs}} V \times dp$$

$$\text{Clapeyron equation: } \frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$$

The Clapeyron equation tells us the slope of any phase boundary in terms of the entropy and volume of the transition. It is an exact equation and applies to any phase equilibrium of any pure substance.



## The solid-liquid boundary



$\Delta_{\text{fus}}H$  – a molar enthalpy change accompanying melting (fusion) at temperature  $T$ .

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}H/T \quad \frac{dp}{dT} = \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}$$

$\Delta_{\text{fus}}H$  is positive (the only exception is helium-3) and  $\Delta_{\text{fus}}V$  is usually positive and always small  $\Rightarrow$  the slope  $dp/dT$  is steep and usually positive. We can obtain the formula for the phase boundary by integration assuming that  $\Delta_{\text{fus}}H$  and  $\Delta_{\text{fus}}V$  change very little and can be

$$\int_{p^*}^p dp = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \int_{T^*}^T \frac{dT}{T} \quad p \approx p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T}{T^*}$$

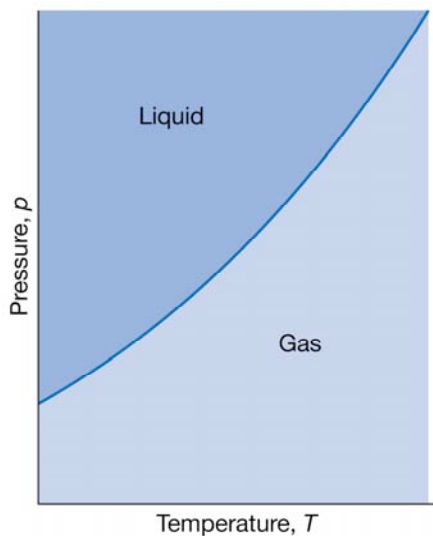
When  $T$  is close to  $T^*$ , the logarithm can be approximated:

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

(because  $\ln(1+x) = x - (1/2)x^2 + (1/3)x^3 + \dots \approx x$  if  $x \ll 1$ )

$$p \approx p^* + \frac{\Delta_{\text{fus}}H}{T^* \Delta_{\text{fus}}V} (T - T^*)$$

## The liquid-vapor boundary



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

$\Delta_{\text{vap}}H$  is positive and  $\Delta_{\text{vap}}V$  is large and positive –  $dp/dT$  is positive but is much smaller than for the solid-liquid boundary.  $dT/dp$  is large – the boiling temperature is more responsive to pressure than the freezing temperature.

*Example 2. Estimating the effect of pressure on the boiling temperature.*

Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

At the boiling point  $\Delta_{\text{vap}}H/T$  is Trouton's constant,  $85 \text{ J K}^{-1} \text{ mol}^{-1}$ . Because the molar volume of gas is much greater than the molar volume of liquid,

$$\Delta_{\text{vap}}V = V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{l}) \approx V_{\text{m}}(\text{g})$$

The molar volume of a perfect gas is about  $25 \text{ L mol}^{-1}$  at 1 atm.

$$dp/dT \approx (85 \text{ J K}^{-1} \text{ mol}^{-1}) / (25 \text{ L mol}^{-1}) = 3.4 \times 10^3 \text{ Pa K}^{-1} = 0.034 \text{ atm K}^{-1}$$

$$dT/dp = 29 \text{ K atm}^{-1}$$

A change of pressure of +0.1 atm changes a boiling temperature by about 3 K.

$$\Delta_{\text{vap}}V \approx V_{\text{m}}(\text{g}) \quad V_{\text{m}}(\text{g}) = RT/p \quad \frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T(RT/p)} = \frac{p\Delta_{\text{vap}}H}{RT^2}$$

$$\frac{dp}{pdT} = \frac{\Delta_{\text{vap}}H}{RT^2} \quad \frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}}H}{RT^2} \text{ - Clausius-Clapeyron equation}$$

$$\frac{d \ln p}{dT/T^2} = \frac{\Delta_{\text{vap}}H}{R} \quad \frac{d \ln p}{d(1/T)} = -\frac{\Delta_{\text{vap}}H}{R}$$

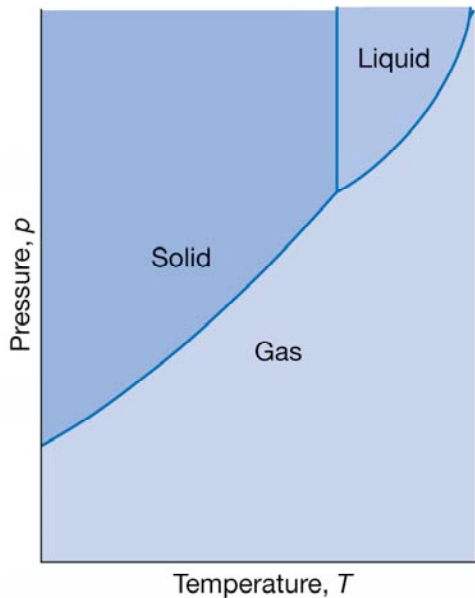
$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

This equation can be used to estimate the vapor pressure of liquid at any temperature from its normal boiling point, the temperature at which is 1 atm (760 Torr). For example, the normal boiling point of benzene is 80°C (353 K) and  $\Delta_{\text{vap}}H = 30.8 \text{ kJ mol}^{-1}$

To calculate the vapor pressure at 20°C (293 K):

$$\chi = (30800 \text{ J mol}^{-1} / 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) / \{1/(293 \text{ K}) - 1/(353 \text{ K})\}$$

Using the result for  $\chi$  and  $p^* = 760 \text{ Torr}$ , we obtain  $p = 89 \text{ Torr}$  (the experimental value is 75 Torr).



### The solid-vapor boundary

The only difference between this case and the liquid-vapor boundary – the enthalpy of vaporization is replaced by the enthalpy of sublimation,  $\Delta_{\text{sub}}H$ . Because  $\Delta_{\text{sub}}H > \Delta_{\text{vap}}H$ , the Clausius equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet.

### The Ehrenfest classification of phase transitions

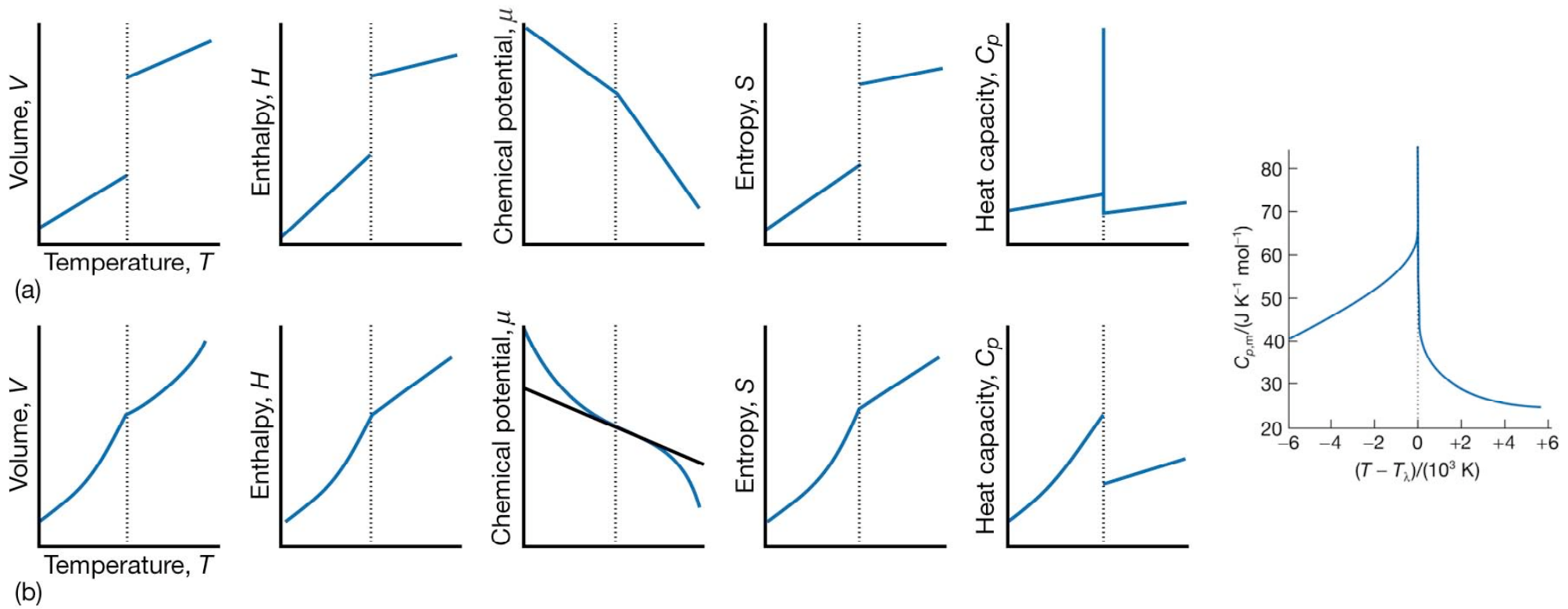
There are many different types of phase transitions. They can be classified using thermodynamic properties of substances, in particular, the behavior of the chemical potential – the **Ehrenfest classification**.

Many phase transitions (like fusion and vaporization) are accompanied by the changes of entropy and volume. These changes affect the slopes of the chemical potentials of the phases at either side of the phase transition.

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

Because  $\Delta_{\text{trs}}V$  and  $\Delta_{\text{trs}}H$  are nonzero for melting and vaporization, the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition – the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition – such transitions are classified as **first-order transitions**.





$C_p$  is the slope of a plot of  $H$  vs.  $T$ . At a first-order phase transition,  $H$  changes by a finite amount for an infinitesimal change of temperature – at the transition temperature the heat capacity is infinite. The physical reason – heating drives the transition rather than raising the temperature. Boiling water stays at the same temperature even though heat is being supplied.

A **second-order transition** – the first derivative of  $\mu$  is continuous but its second derivative is discontinuous. The volume and entropy (and hence the enthalpy) do not change at the transition. The heat capacity is discontinuous but does not become infinite. Example – the conducting-superconducting transition in metals at low temperatures.

**$\lambda$ -transition** – a phase transition that is not first-order yet the heat capacity becomes infinite at the transition temperature. The heat capacity of the system begins to increase well before the transition. This type includes order-disorder transitions in alloys, the onset of ferromagnetism, and the fluid-superfluid transition in He.