

# Phase Transitions and Phase Diagrams

## One-component systems

Enthalpy and entropy dependence on P and T

Gibbs free energy dependence on P and T

Clapeyron equation

Understanding phase diagrams for one-component systems

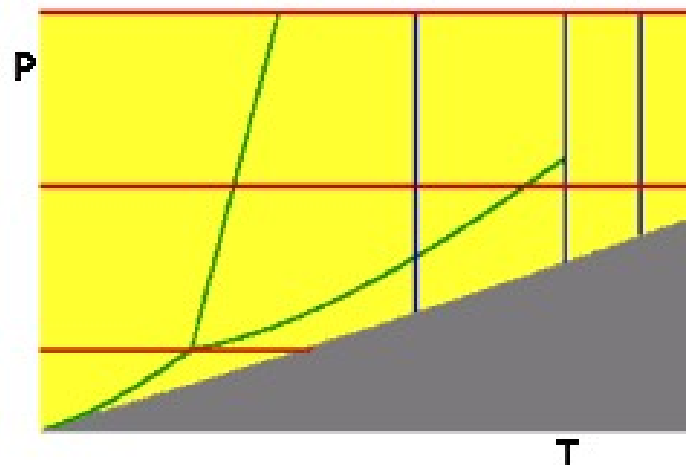
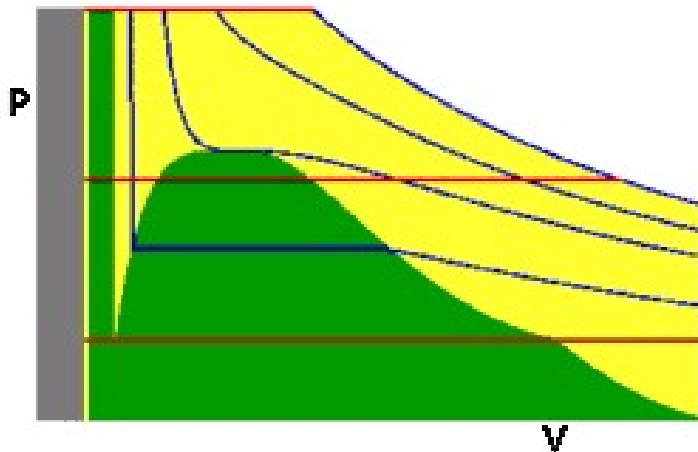
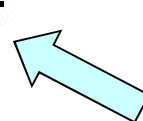
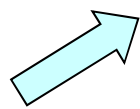
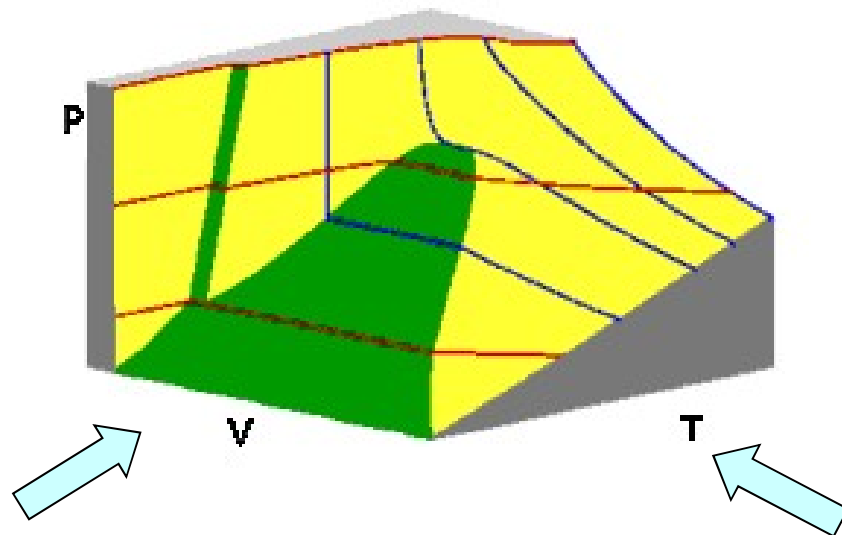
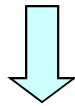
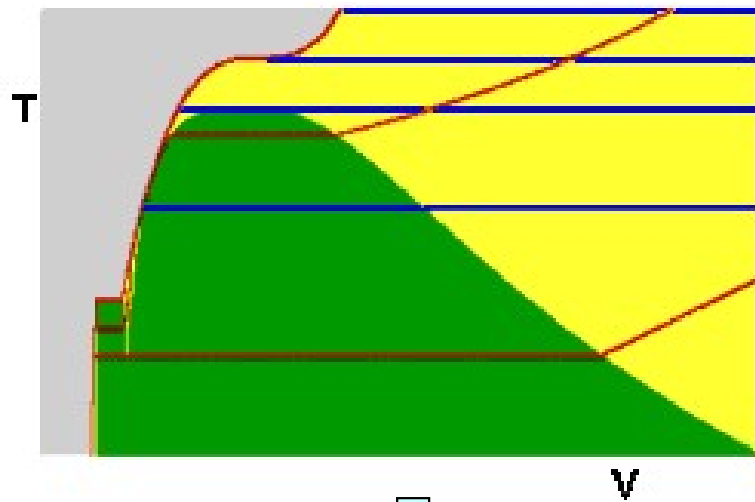
Polymorphic phase transitions

Driving force for a phase transition

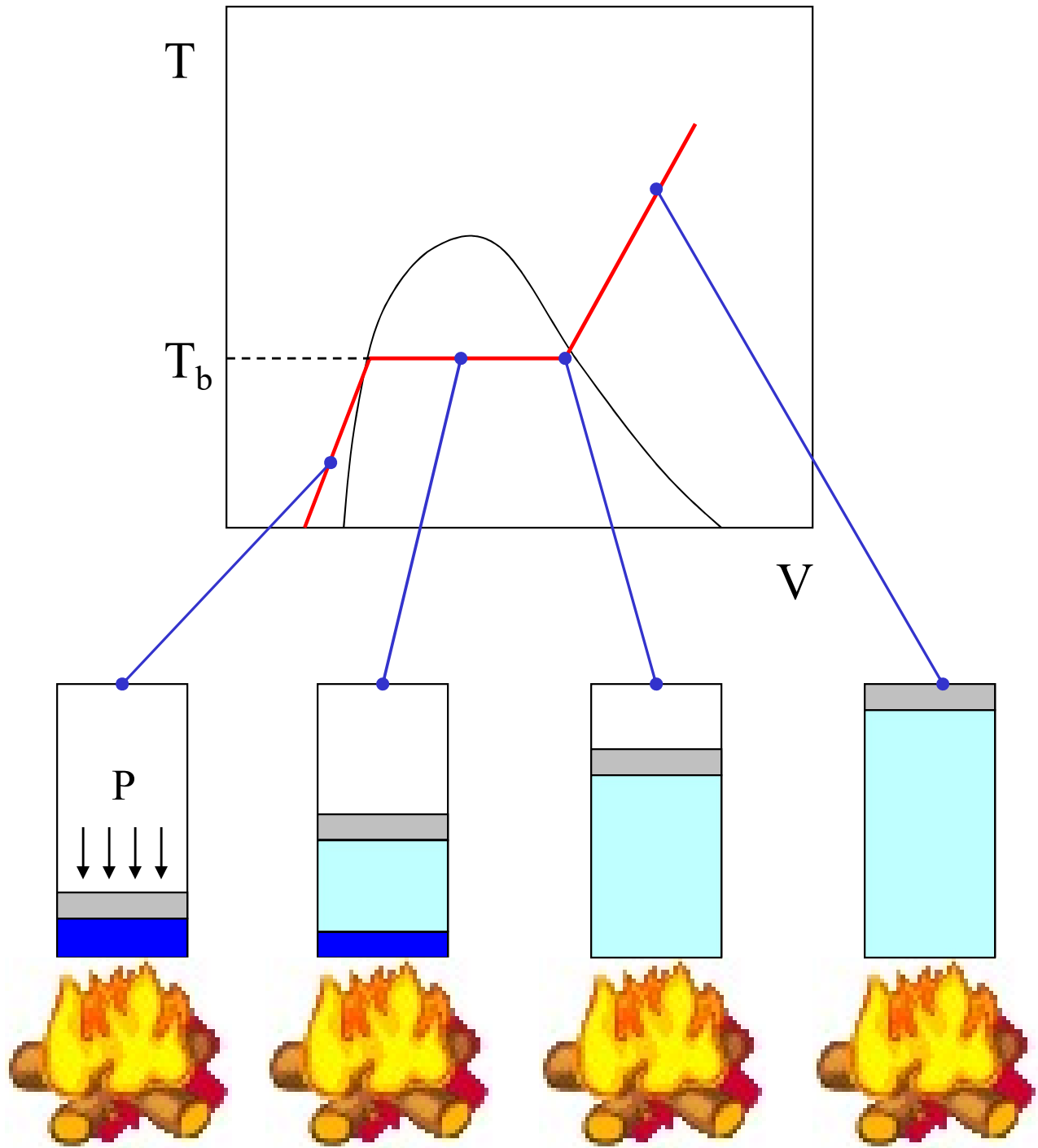
First order and second-order phase transitions

**Reading:** 1.2 of Porter and Easterling  
Chapter 7.1 – 7.4 of Gaskell

# PVT Surface of a Pure Substance



# A pure substance is heated at constant pressure



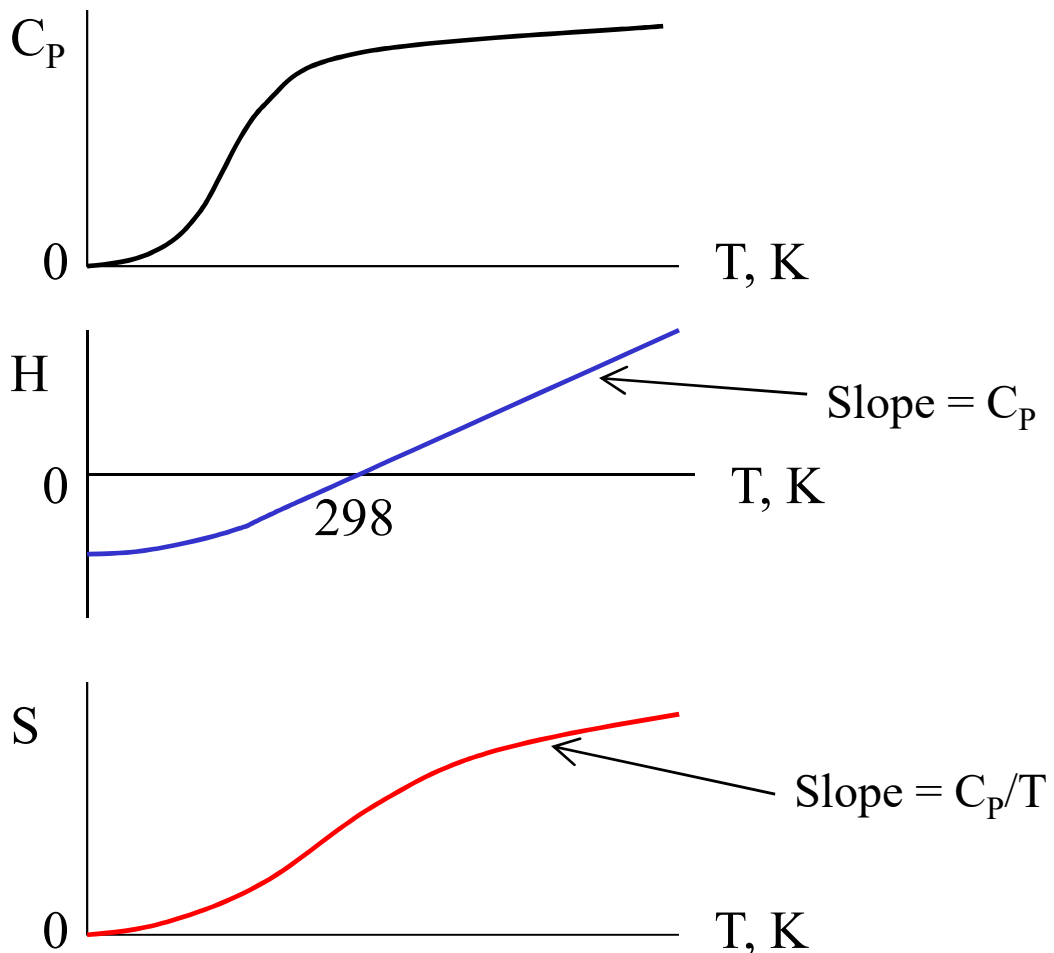
## H and S as function of T at constant P

In a closed one-component system equilibrium, at temperature  $T$  and pressure  $P$ , corresponds to the state with minimum Gibbs free energy  $G$ . Therefore, in order to predict what phases are stable under different conditions we have to examine the dependence of  $G$  on  $T$  and  $P$ .

Let's use thermodynamic relations to predict the temperature dependence of  $H$ ,  $S$ , and  $G$  at constant  $P$ .

For  $H(T)$  we have  $\left(\frac{\partial H}{\partial T}\right)_P = C_P$        $H(T) = H_{298} + \int_{298}^T C_P dT$

For  $S(T)$  we have  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$        $S(T) = \int_0^T \frac{C_P}{T} dT$

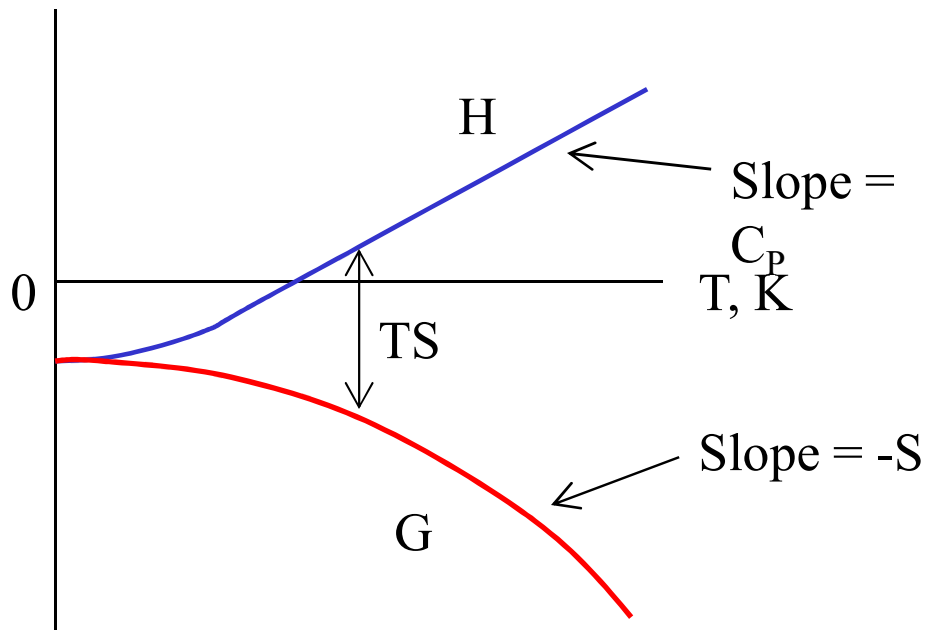


## G as function of T at constant P

For  $G = H - TS$  we have  $dG = -SdT + VdP$  and for  $P = \text{const}$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{for the slope}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_P}{T} \quad \text{for the curvature}$$



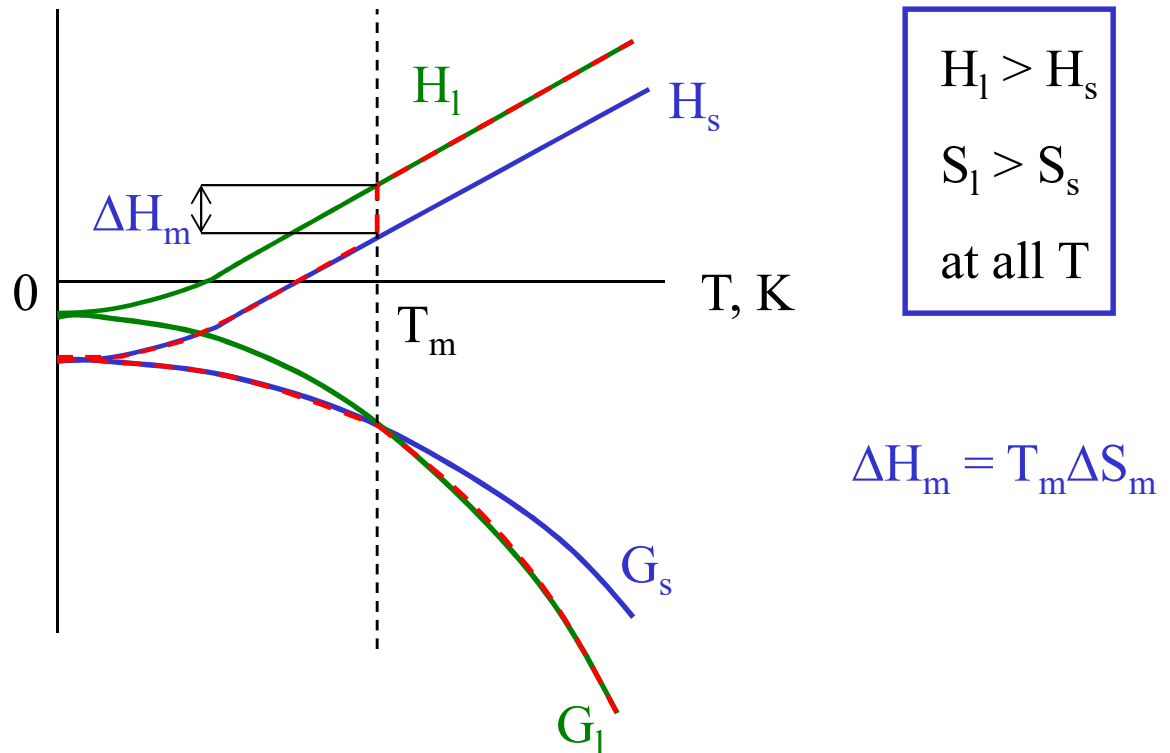
$G(T)$  for a single phase at  $P = \text{const}$

## G as function of T at constant P for liquid and solid phases

At all temperatures the liquid has a higher internal energy  $U$  and enthalpy  $H$  as compared to the solid. Therefore  $G_l > G_s$  at low  $T$ .

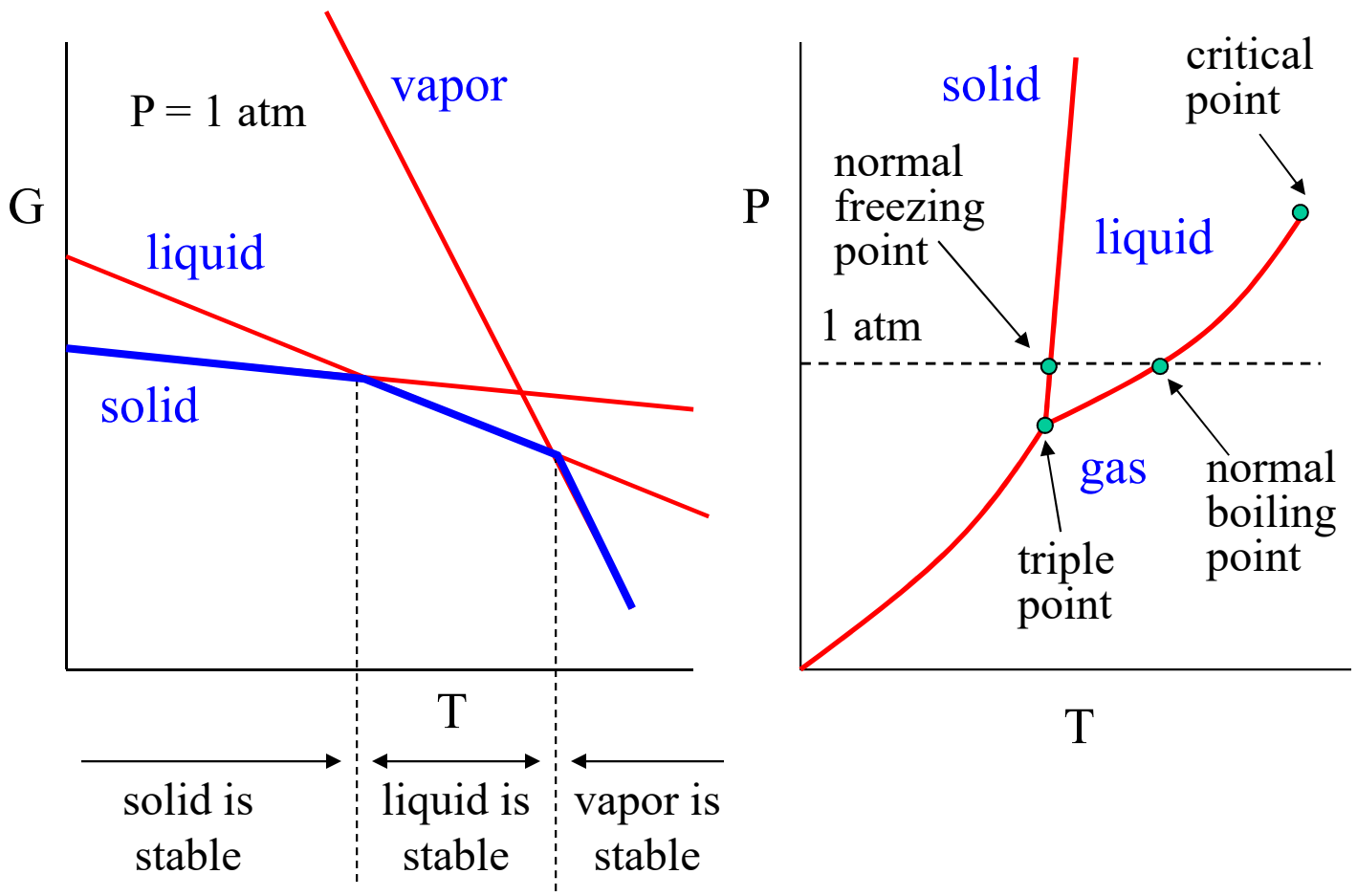
The liquid phase, however, has a higher entropy  $S$  than the solid phase at all  $T$ . Therefore  $G_l$  decreases more rapidly with  $T$  as compared to  $G_s$ .

At  $T_m$   $G_l(T)$  crosses  $G_s(T)$  and both liquid and solid phases can co-exist in equilibrium ( $G_l = G_s$ )



At  $T_m$  the heat supplied to the system will not rise its temperature but will be used to supply the latent heat of melting  $\Delta H_m$  that is required to convert solid into liquid. **At  $T_m$  the heat capacity  $C_p = (\partial H/\partial T)_p$  is infinite** – addition of heat does not increase  $T$ .

## A typical P-T phase diagram for a pure material



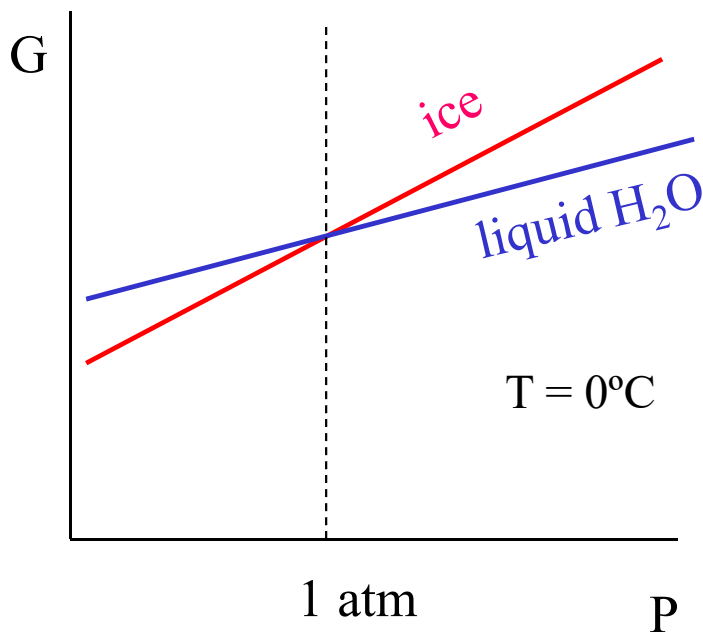
The red lines on the phase diagram show the conditions where different phases coexist in equilibrium:  $G_{\text{phase1}} = G_{\text{phase2}}$

## G as function of P at constant T for liquid and solid phases

As we can see from the fundamental equation,  $dG = VdP - SdT$ , the free energy of a phase increases with pressure:

$$\left(\frac{\partial G}{\partial P}\right)_T = V > 0$$

If the two phases have different molar volumes, their free energies will increase by different amounts when pressure changes at a fixed T.



$$V_l < V_s \text{ for water}$$

$$V_l > V_s \text{ for most materials}$$

How the unusual change of  $V$  upon melting of water could be related to ice-skating?

What is the curvature of the  $G(P)$  at constant  $T$ ?

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad \text{- isothermal compressibility}$$

$$B = -V \left(\frac{\partial P}{\partial V}\right)_T \quad \text{- bulk modulus}$$



## Equilibrium between two phases: Clapeyron equation

If two phases in equilibrium have different molar volumes, their free energies will increase by different amounts when pressure changes at a fixed T. The equilibrium, therefore will be disturbed by the change in pressure. The only way to maintain equilibrium at different pressures is to change temperature as well.

For two phases in equilibrium  $G_l = G_s$  and  $dG_l = dG_s$  for infinitesimal change in T and P (so that the system remains in equilibrium)

$$dG_l = V_l dP - S_l dT$$

$$dG_s = V_s dP - S_s dT$$

$$V_l dP - S_l dT = V_s dP - S_s dT$$

$$\left( \frac{dP}{dT} \right)_{\text{eq.}} = \frac{S_s - S_l}{V_s - V_l} = \frac{\Delta S}{\Delta V}$$

$$\text{At equilibrium} \quad \Delta G = \Delta H - T \Delta S = 0 \quad \text{and} \quad \Delta H = T \Delta S$$

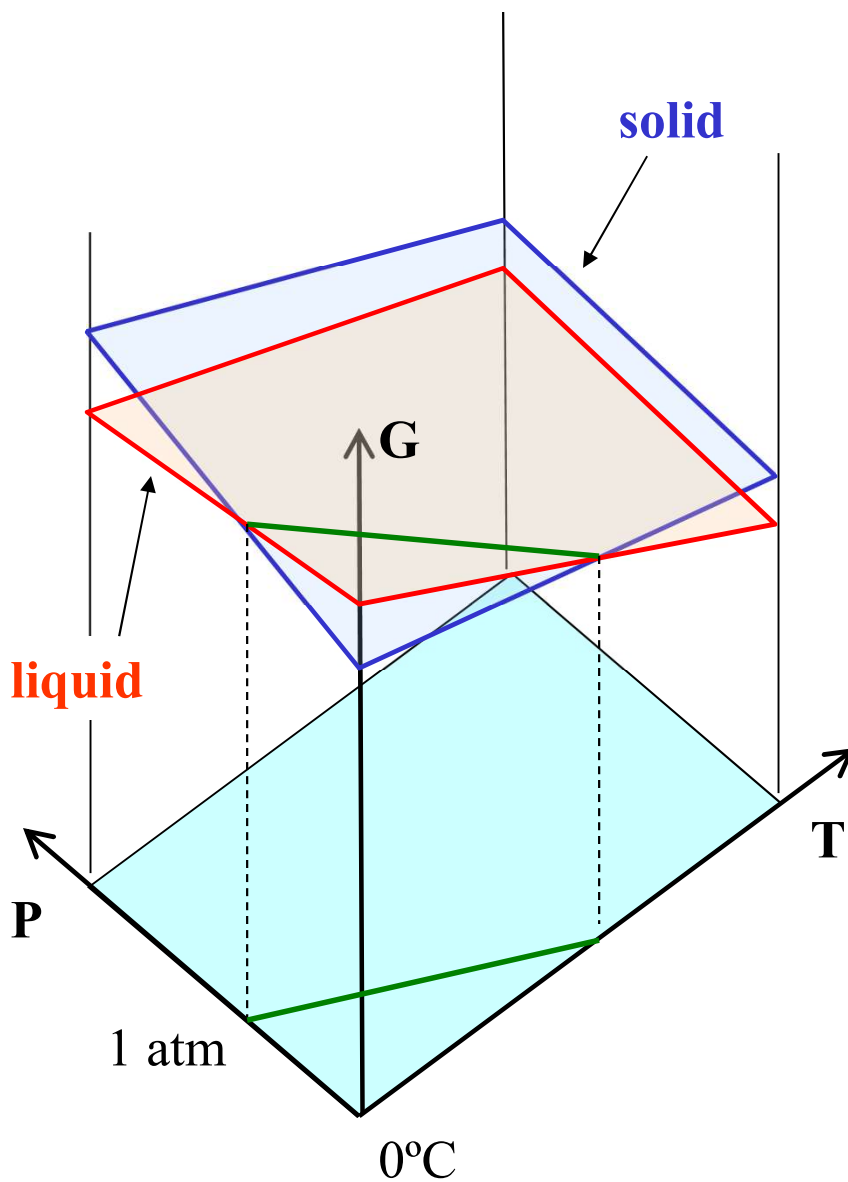
Therefore  $\boxed{\left( \frac{dP}{dT} \right)_{\text{eq.}} = \frac{\Delta H}{T \Delta V}}$  - the Clapeyron equation

The Clapeyron equation gives the relationship between the variations of pressure and temperature required for maintaining equilibrium between the two phases.

## G as function of P and T for liquid and solid phases

Schematic representation of the equilibrium surfaces of the solid and liquid phases of water in G-T-P space.

The planes show the free energies of liquid and solid phases, the intersections of the planes correspond to the (P, T) conditions needed for maintaining equilibrium between the phases,  $G_l = G_s$ .



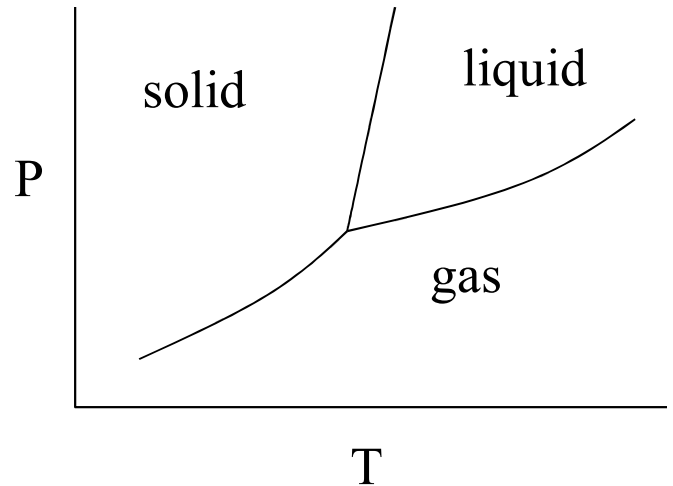
## Clapeyron equation: examples

A typical diagram for a pure material:

**For liquid to gas transition:**  $\Delta V = V_g - V_l \gg 0$

$\Delta H = H_g - H_l > 0$  – we have to add heat to convert liquid to gas.

Therefore 
$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V} > 0$$

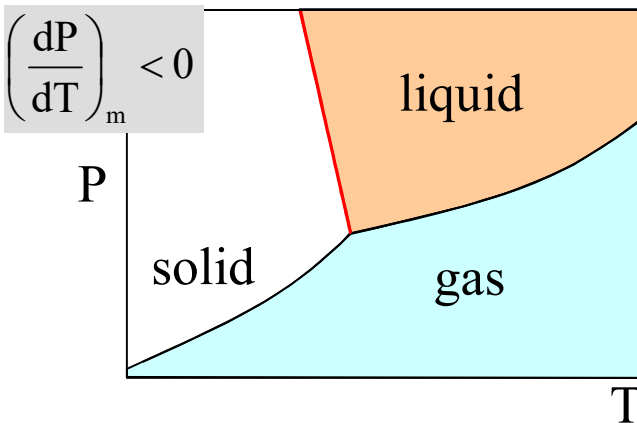


**For liquid to solid transition:**  $\Delta V = V_s - V_l < 0$  for most materials

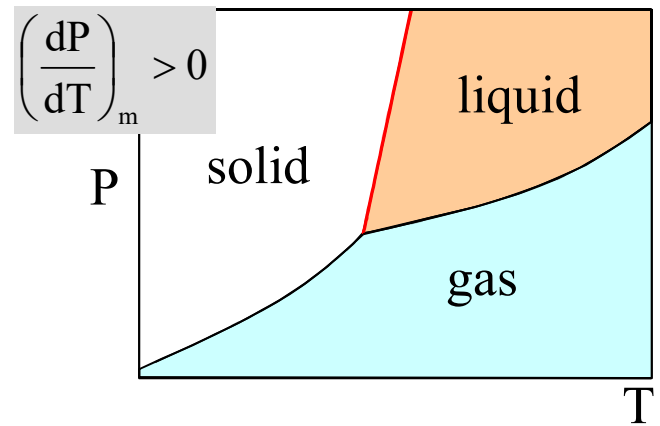
$\Delta H = H_s - H_l < 0$  – heat is released upon crystallization.

Therefore 
$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V} > 0$$

For some materials, however,  $\Delta V = V_s - V_l > 0$  and  $\left(\frac{dP}{dT}\right)_{\text{eq.}} < 0$



Si, Ge, Ga, Bi, GaAs, diamond ...



Fe, Ni, Au, CuZn, Ar, ...

In general, it takes heat ( $\Delta H > 0$ ) to proceed from a low-temperature to a high-temperature phase (entropy of a high-temperature phase is higher than the entropy of a low-temperature phase). **Therefore, the slope of the equilibrium lines in a P-T phase diagram of a pure material reflects the relative densities of the two phases.**

## Clapeyron equation: more examples

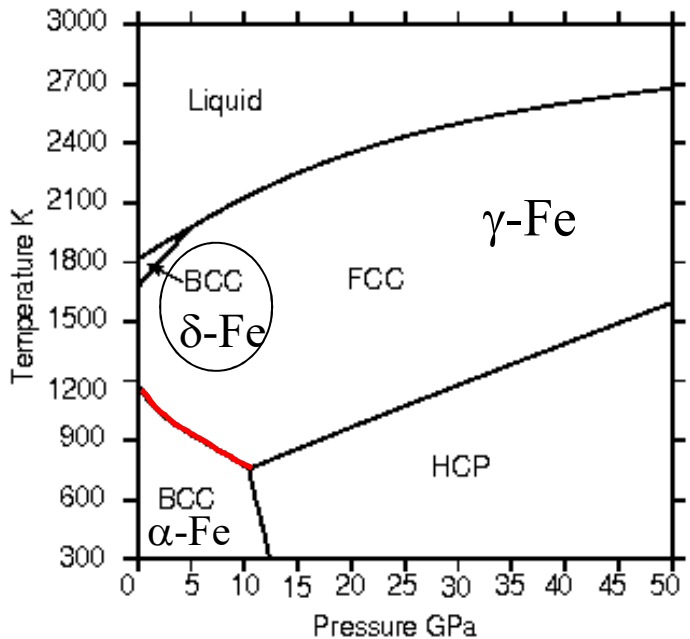
Some materials may exist in more than one crystal structure, this is called **polymorphism**. If the material is an elemental solid, it is called **allotropy**.

The diagram shows the stable phases for pure iron at varying temperature and pressure.

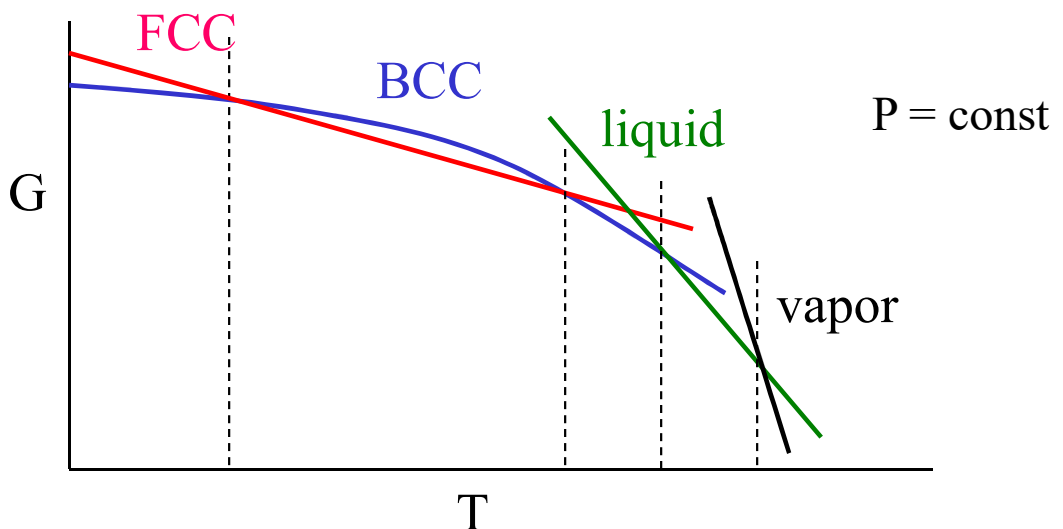
Close-packed FCC  $\gamma$ -Fe has a smaller molar volume than BCC  $\alpha$ -Fe:  $\Delta V = V_{\gamma} - V_{\alpha} < 0$

At the same time  
 $\Delta H = H_{\gamma} - H_{\alpha} > 0$

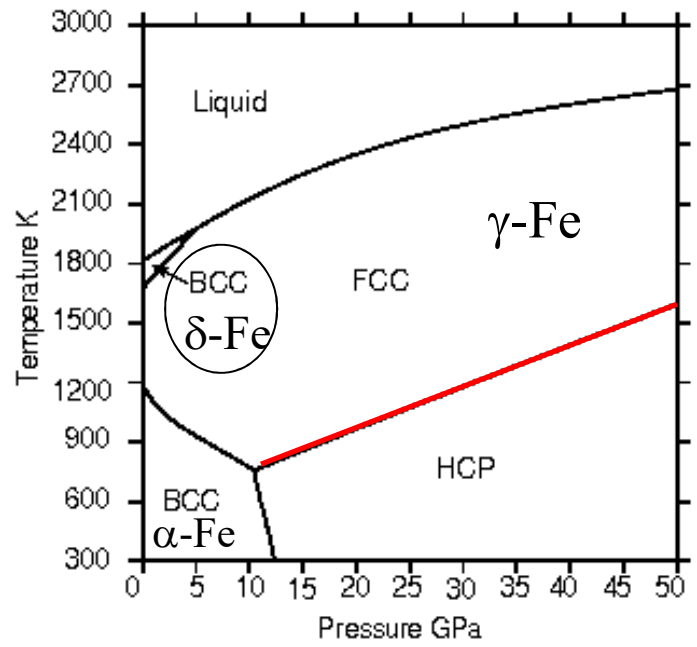
Therefore 
$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V} < 0$$



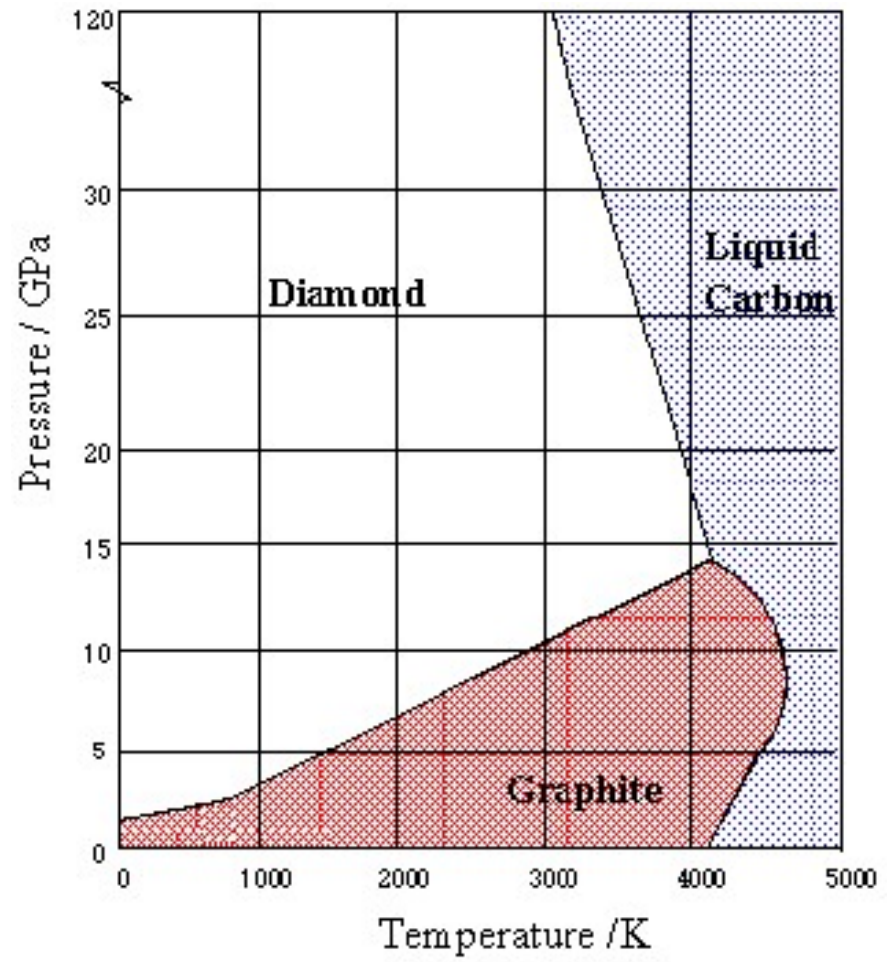
The effect of increasing pressure is to increase the area of the phase diagram over which the phases of the smaller molar volume (higher density) is stable.



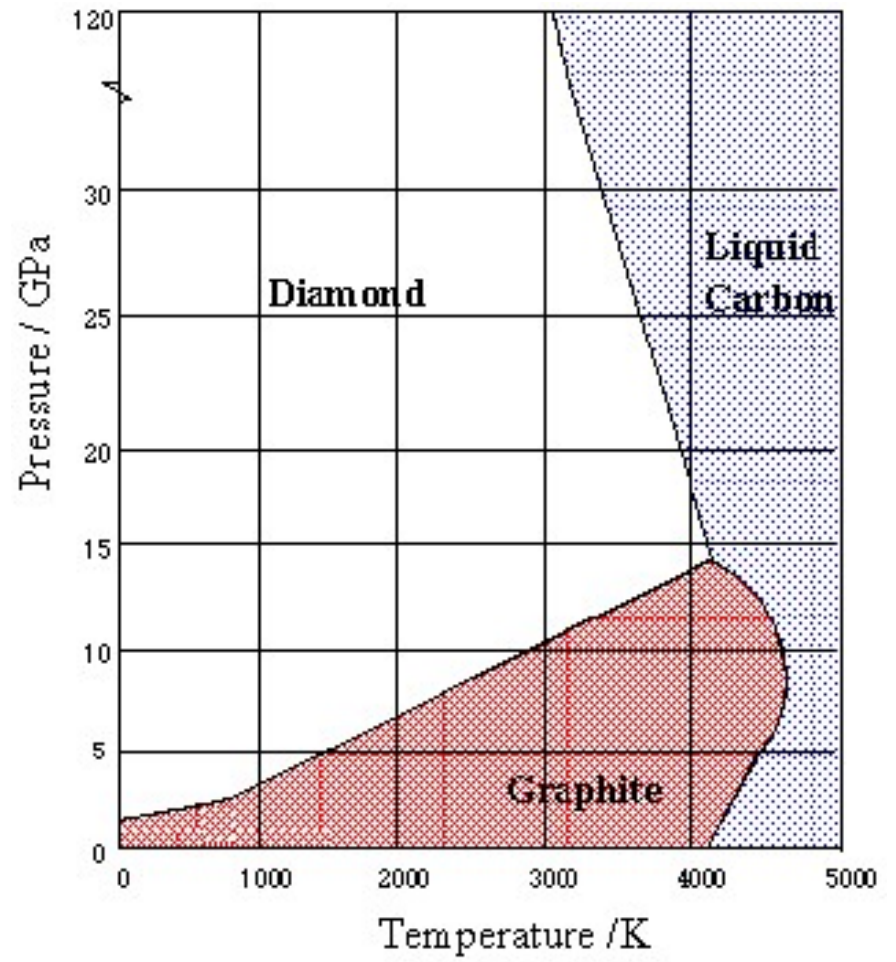
$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V}$$



$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V}$$



$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V}$$



**Can the volume expansion of water upon melting explain ice-skating?**

$$\left(\frac{dP}{dT}\right)_{\text{eq.}} = \frac{\Delta H}{T\Delta V}$$

$$m = 100 \text{ kg}$$

$$V_{\text{ice}} = 19.63 \text{ cm}^3/\text{mol}$$

$$V_{\text{liquid}} = 18.0 \text{ cm}^3/\text{mol}$$

$$\Delta H_m = 5636 \text{ J/mol}$$

skate : 2 mm wide, 1 cm contact length



## **Squeezing diamond from graphite: What pressure should we apply to transform graphite to diamond at 298 K?**

In reference books we can find that at 298 K and 1 atm:

$$H_{\text{diamond}} = 1900 \text{ J/mol}$$

$$S_{\text{graphite}} = 5.73 \text{ J/K}$$

$$S_{\text{diamond}} = 2.43 \text{ J/K}$$

$$\rho_{\text{graphite}} = 2.22 \text{ g/cm}^3$$

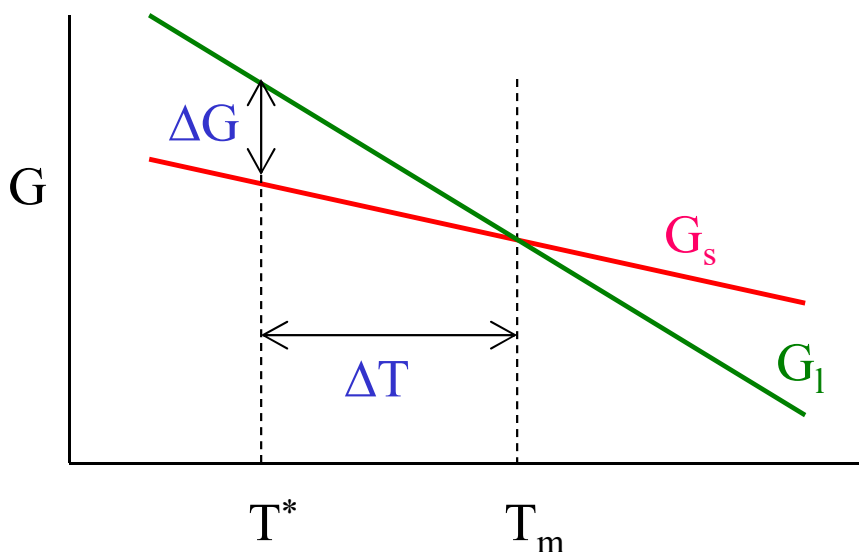
$$\rho_{\text{diamond}} = 3.515 \text{ g/cm}^3$$

## The driving force for the phase transformation

If solid and liquid are in equilibrium,  $G_s = G_l$  and a *slow* addition of heat leads to the melting of some part of the solid, but do not change the total  $G$  of the system:

$G = n_l G_l + n_s G_s = \text{const}$ , where  $n_l$  and  $n_s$  are the numbers of moles of liquid and solid phases, and  $G_l$  and  $G_s$  are the molar Gibbs free energies.

If energy is added/removed *quickly*, the system can be brought out of equilibrium (overheated or undercooled) – the melting/freezing process is spontaneous/irreversible and  $G$  is decreasing.



For small undercooling  $\Delta T$  we can neglect the difference in  $C_p$  of liquid and solid phases and assume that  $\Delta H$  and  $\Delta S$  are independent of temperature.

**The driving force for solidification**

At temperature  $T^*$

$$G_l = H_l - T^* S_l$$

$$G_s = H_s - T^* S_s$$

$$\Delta G = \Delta H - T^* \Delta S$$

At temperature  $T_m$

$$\Delta G = \Delta H - T_m \Delta S = 0$$

$$\Delta S = \frac{\Delta H_m}{T_m}$$

$$\Delta G \approx \Delta H_m - T^* \frac{\Delta H_m}{T_m}$$

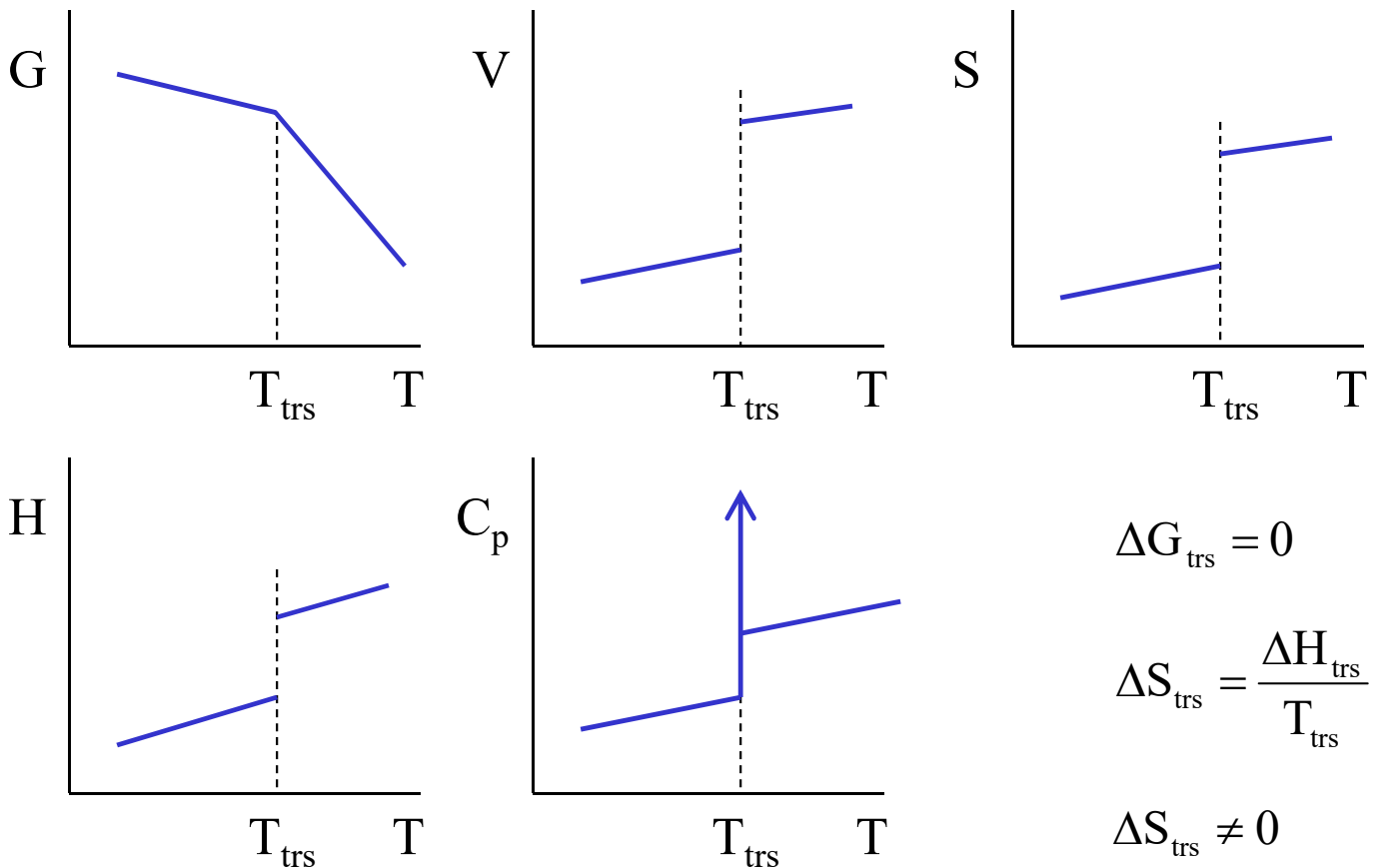
$$\Delta G \approx \frac{\Delta H_m \Delta T}{T_m}$$

## First-order and second-order phase transitions (I)

The classification of phase transitions proposed by Ehrenfest is based on the behavior of  $G$  near the phase transformation.

- **First-order phase transition:** first derivatives of  $G$  are discontinuous.
- **Second-order phase transition:** first derivatives of  $G$  are continuous, but second derivatives of  $G$  are discontinuous.

### First-order phase transition



$$\Delta G_{\text{trs}} = 0$$

$$\Delta S_{\text{trs}} = \frac{\Delta H_{\text{trs}}}{T_{\text{trs}}}$$

$$\Delta S_{\text{trs}} \neq 0$$

$$\Delta H_{\text{trs}} \neq 0$$

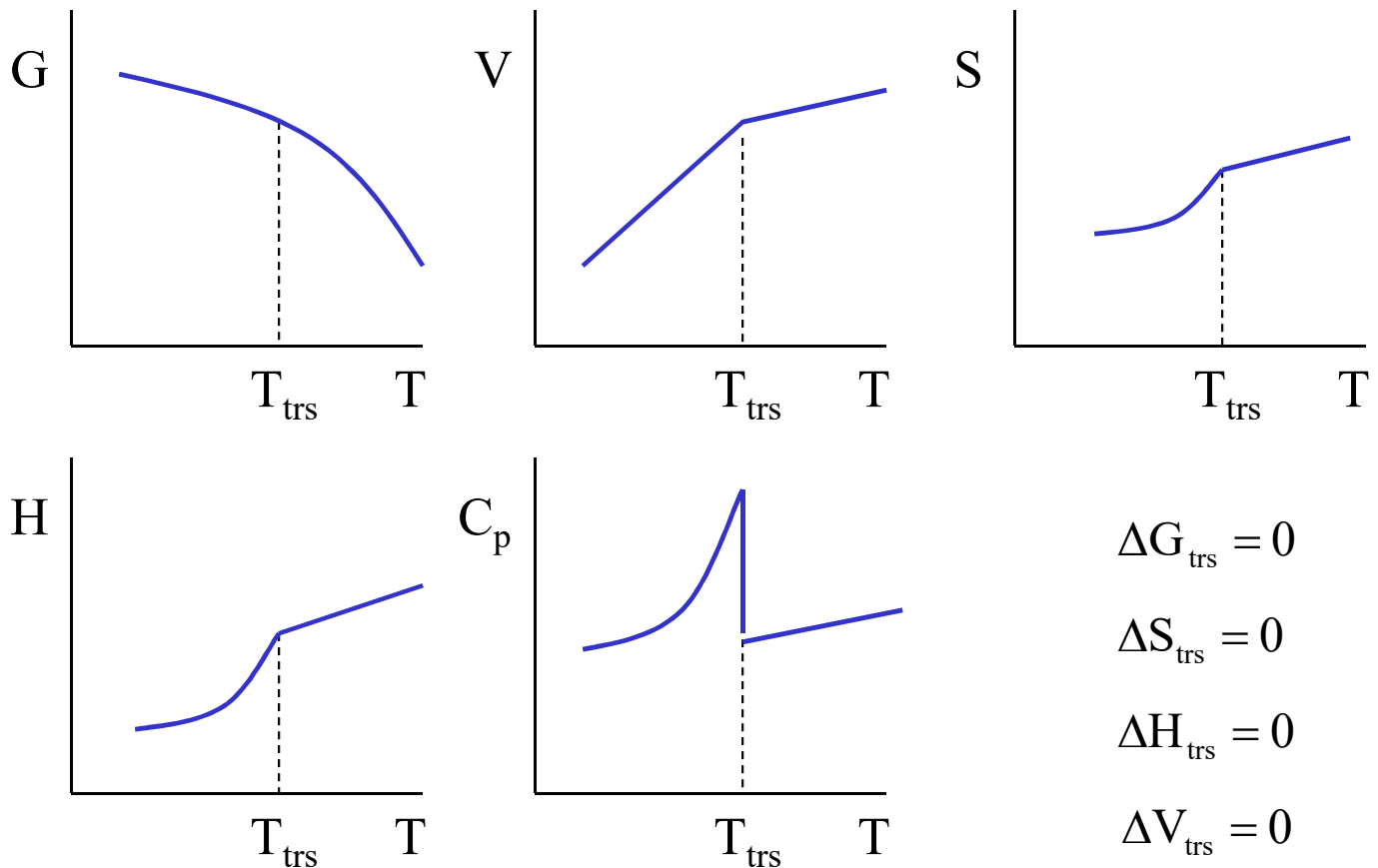
$$C_p = \left( \frac{dH}{dT} \right)_P$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S \quad \left( \frac{\partial G}{\partial P} \right)_T = V \quad - \text{discontinuous}$$

e.g. melting, boiling, sublimation, some polymorphous phase transitions.

## First-order and second-order phase transitions (II)

### Second-order phase transition



$$\Delta G_{\text{trs}} = 0$$

$$\Delta S_{\text{trs}} = 0$$

$$\Delta H_{\text{trs}} = 0$$

$$\Delta V_{\text{trs}} = 0$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$C_P = \left(\frac{dH}{dT}\right)_P$$

- continuous (S and V do not jump at transition)

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial V}{\partial T}\right)_P \quad \left(\frac{\partial^2 G}{\partial P \partial T}\right) = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{- discontinuous}$$

e.g. conducting-superconducting transition in metals at low temperatures.

## Summary

Make sure you understand language and concepts:

- Enthalpy and entropy dependence on P and T
- Gibbs free energy dependence on P and T
- Clapeyron equation
- Understanding phase diagrams for one-component systems
- Driving force for a phase transition
- First order and second-order phase transitions

Make sure you understand P-T, G-P, G-T 2D phase diagrams for a one-component system (what is shown, what are the lines separating different regions, how to predict the slopes of the lines, etc.)