Studiengang Geowissenschaften M.Sc.
Wintersemester 2004/05

Thermodynamics and Phase Transitions in Minerals

Victor Vinograd & Andrew Putnis

Basic thermodynamic concepts

One of the central themes in Mineralogy is the study of *mineral behaviour* - the response of a mineral to changing physical and chemical conditions.

Equilibration always tends to reduce the *free energy* to a minimum.

The internal energy *U,* of a mineral is the potential energy stored in the interatomic bonding + the kinetic energy of the atomic vibrations.

Adding more heat increases the kinetic energy and hence the temperature and the internal energy.

If the crystal is allowed to expand (and hence do some work on its surroundings) the total change in the internal energy is:

$$dU = \underbrace{dQ}_{\text{Change in heat content}} - \underbrace{PdV}_{\text{Work done in expansion}}$$

It is also convenient to define another energy function called the *enthalpy* H

as $$H = U + PV$$

Heat Capacity

A fundamental property of a material is its *heat capacity* C which describes the amount of heat dQ, required to change the temperature of one mole of the material by

$$C = dQ/dT$$

The heat capacity can be defined at constant volume (or at constant pressure) :

From $dU = dQ - PdV$

$$dU/dT = dQ/dT - P\,dV/dT$$

At constant volume $dV/dT = 0$

and $(dU/dT)_V = (dQ/dT)_V = C_V$

The heat capacity can also be defined at constant pressure :

From $H = U + PV$

$$dH = dU + PdV + VdP$$

Since $dU = dQ - PdV$

$$dH = dQ + VdP$$

$$dH/dT = dQ/dT + VdP/dT$$

At constant pressure $dP/dT = 0$

and $(\mathrm{dH/dT})_\mathrm{P} = (\mathrm{dQ/dT})_\mathrm{P} = \mathrm{C}_\mathrm{P}$

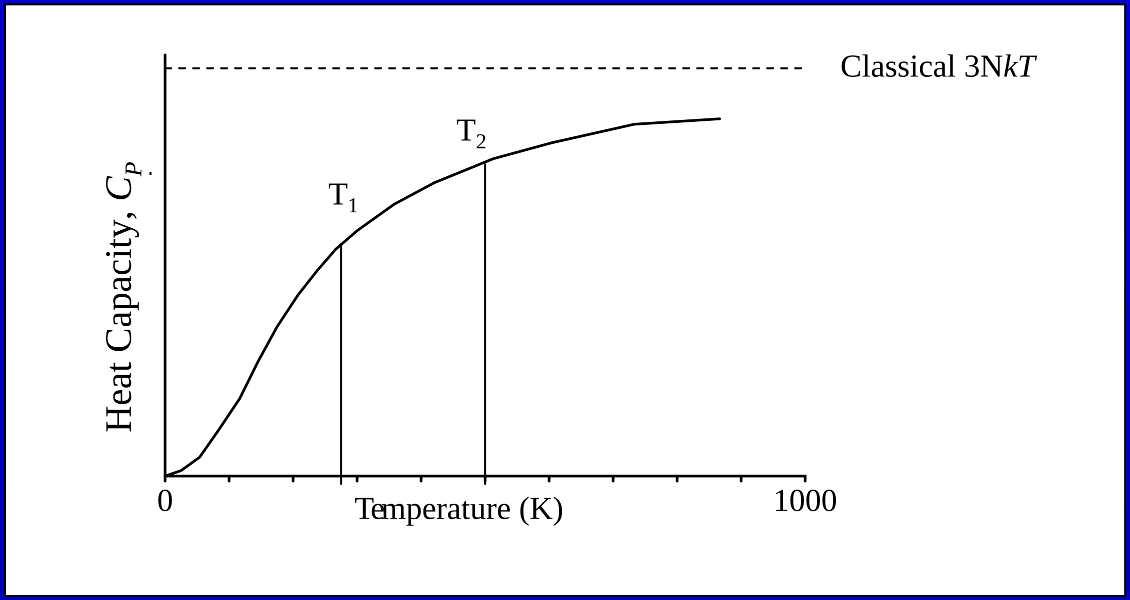
In experiments it is easier to consider constant pressure rather than constant volume, and so enthalpy changes are easier to measure than internal energy changes.

Enthalpy is analogous to internal energy at constant pressure i.e. heat input is equal to the enthalpy change if the pressure is constant.

$C_P - C_V = TV\alpha^2/\beta$ where α is the thermal expansion coefficient and β is the compressibility.

$C_P - C_V$ is a very small quantity and becomes significant only at high T.

Variation in heat capacity C_P with temperature.



The enthalpy change between T_1 and T_2 is given by

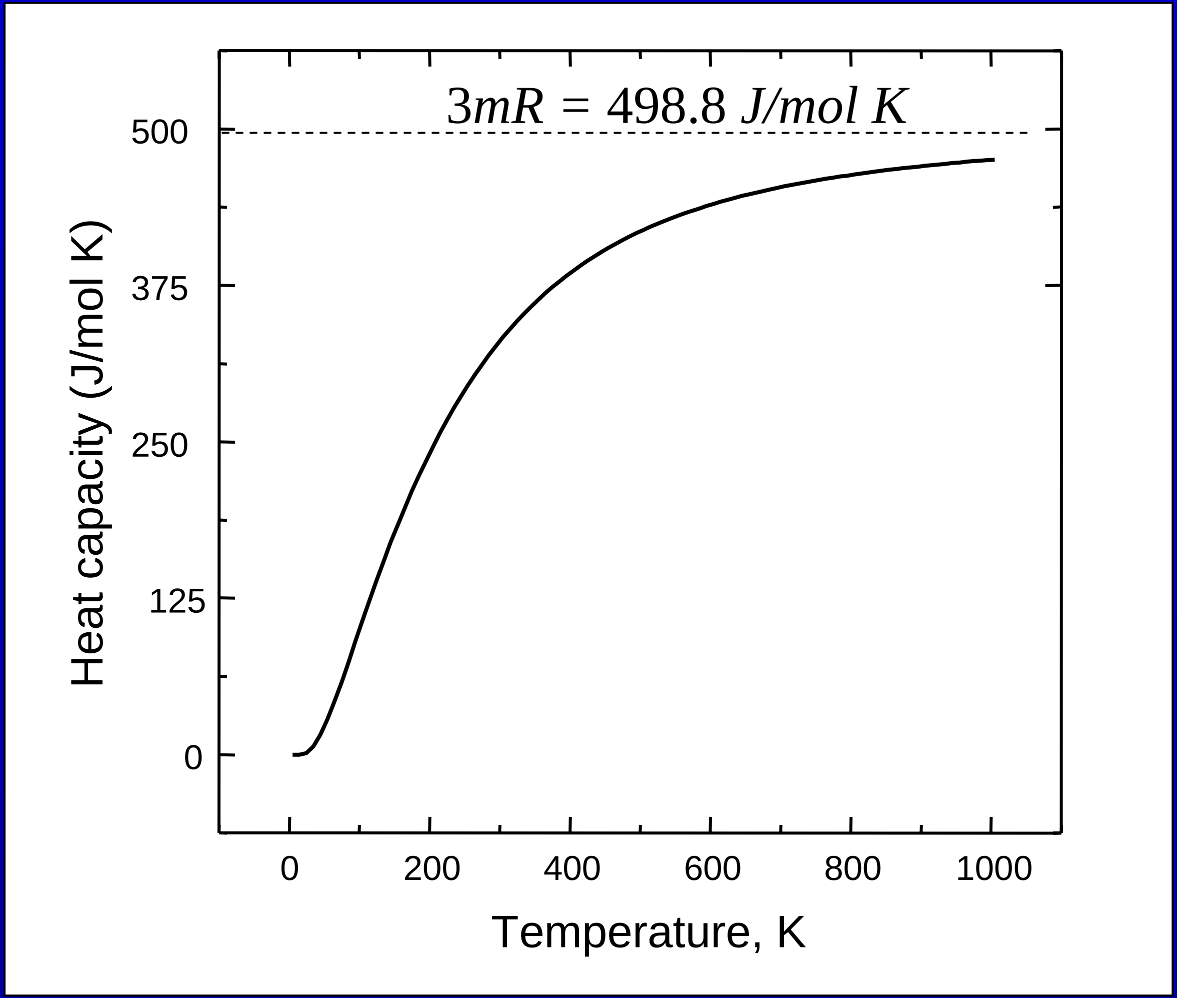
$$H = H_{T_1} + \int_{T_1}^{T_2} C_P \, dT$$

The enthalpy at T_1

$$H = H_0 + \int_{0}^{T_1} C_P \, dT$$

H_0 includes the enthalpy due to potential energy of the crystal at 0K as well as the zero point vibrational energy

The heat capacity of pyrope



Pyrope

$Mg_3Al_2Si_3O_{12}$

$m=3+2+3+12=20$

Enthalpy changes in mineral transformations and reactions

Meaning of *standard states :* 298K and 1 atm P

Enthalpies are defined as the enthalpy of formation from the elements (enthalpies of elements assigned to be zero at the standard state). For ternary oxides enthalpies of formation are often listed from component oxides.

e.g. $Mg + 1/2O_2 \Rightarrow MgO$ at 1 atmosphere and 298K

$$\Delta H_o = -601.5 \text{ kJ/mol.}$$

$$Si + O_2 \Rightarrow SiO_2 \text{ (low quartz)}$$

$$\Delta H_o = -910.7 \text{ kJ/mol.}$$

$$2Mg + Si + 2O_2 \Rightarrow Mg_2SiO_4$$

$$\Delta H_o = -2170.39 \text{ kJ/mol.}$$

(all *exothermic).*

Exercise : Using Hess's Law calculate the enthalpy of formation of olivine from the oxides at 1 atm and 298K (-56.69 kJ/mol)

Enthalpy changes during a polymorphic transformation

If ΔH is positive heat is absorbed i.e. endothermic
If ΔH is negative heat is given out i.e. exothermic

For example: tridymite to quartz

$$Si + O_2 \Rightarrow SiO_2 \text{ (tridymite)}$$

$$\Delta H_f^o = -907.5 \text{ kJ/mol}$$

$$Si + O_2 \Rightarrow SiO_2 \text{ (low quartz)}$$

$$\Delta H_f^o = -910.7 \text{ kJ/mol}$$

$$SiO_2 \text{ (tridymite)} \Rightarrow Si + O_2 \Rightarrow SiO_2 \text{ (low quartz)}$$

$$\Delta H = + 907.5 - 910.7 = -3.2 \text{ kJ/mol}$$

i.e. exothermic

Calcium carbonate $CaCO_3$: calcite and aragonite

The standard state enthalpy of calcite is -1207.37 kJ/mol

The standard state enthalpy of aragonite is -1207.74 kJ/mol

Therefore the transformation from aragonite to calcite involves an enthalpy *increase* of 0.37 kJ/mole i.e. endothermic

But calcite is more stable than aragonite at 25^{o}C and 1 atm. pressure, showing that a *reduction in enthalpy is not a criterion for an increase in stability*

The concept of Entropy

When a mineral changes from one structure to another it exchanges heat with its surroundings. The *entropy* is defined as the quantity which measures the change in the state of order associated with this process. The overall entropy change is the sum of the entropy change in the mineral (i.e. the system under consideration) and the entropy change in the surroundings, i.e.

$$dS = dS_{\text{system}} + dS_{\text{surr.}}$$

For a reversible reaction , i.e. one which passes through a continuous sequence of equilibrium states, $dS = 0$, but for any natural reaction proceeding towards equilibrium, $dS > 0$, according to the Second Law of Thermodynamics.

Entropy

The entropy change is defined by

$$dS > dQ/T$$

where dQ is the amount of heat exchanged by the system at temperature T. In a system free to exchange heat with its surroundings the change in entropy of the system is related to the enthalpy change by the relation

$$dS > dH/T$$

noting that at constant pressure $dQ = dH$.

Thus the criterion for a mineral transformation or reaction to proceed is that

$$dH - TdS < 0.$$

If $dH - TdS = 0$ no further change is possible, i.e. the system is at equilibrium. If
$dH - TdS$ is > 0 the reaction will not proceed.

Entropy and the direction of change in a reaction

The quantity ($dH - TdS$) therefore can be used to define a criterion for the direction of change in a mineral reaction and a definition of equilibrium. This quantity is known as the change in the *Gibbs free energy*, dG of the system. Thus

$$dG = dH - TdS$$

or

$$G = H - TS$$

Therefore the change in free energy ΔG must always be negative in a reaction. Equilibrium is defined as the state with the minimum Gibbs free energy.

Configurational entropy and disorder

In the statistical definition, according to Boltzmann, the entropy of a system in a given state is related to the probability of the existence of that state. The "state" in this context refers to a particular distribution of atoms and their vibrational energy levels. Mathematically this is expressed as

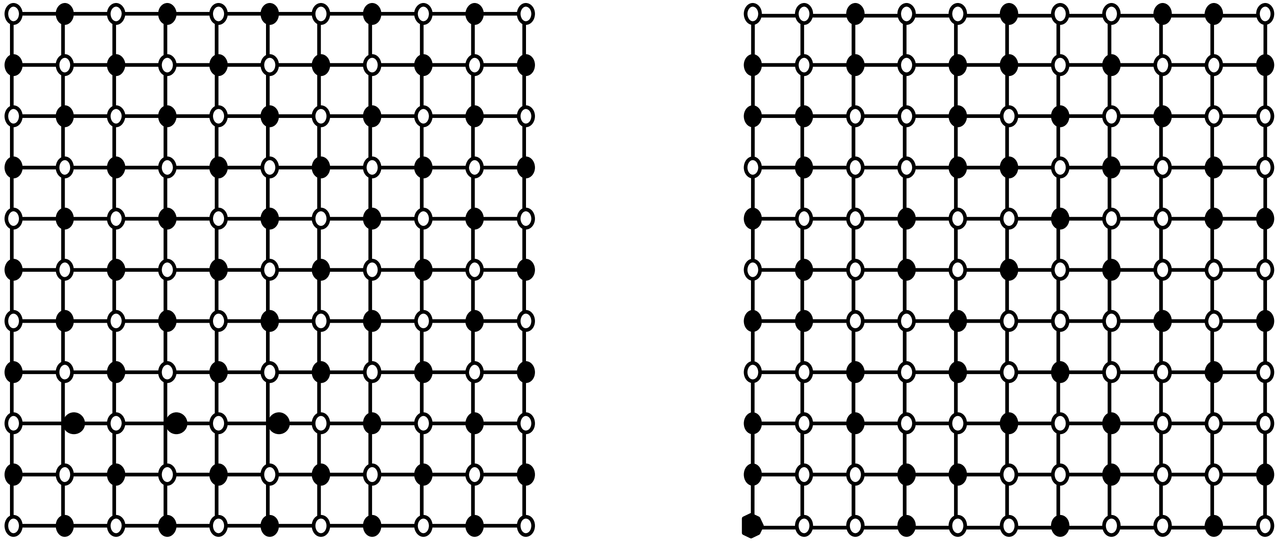
$$S = k \ln \omega$$

where ω is the probability that a given state will exist and k is Boltzmann's constant (1.38 x 10^{-23} JK^{-1})

The probability is related to the state of disorder or randomness in the structure which may be expressed statistically by the number of different ways in which atoms can arrange themselves in that state.

Entropy - an example

Consider a distribution of atoms of A and B on a simple cubic lattice which contains a total of *N* atomic sites.



Ordered

Disordered

To determine the entropy of a completely random distribution of A and B atoms we need to calculate the number of ways in which the atoms can be arranged

If the atomic fraction of A atoms is x_A and of B atoms is x_B, there are $x_A N$ atoms of A and $x_B N$ atoms of B to be distributed over N sites. The number of such arrangements, ω, is determined from statistics as

$$\omega = N! / (x_A N)!\,(x_B N)!$$

The entropy associated with this disorder is therefore

$$S = k \ln \omega = k \ln [N! / (x_A N)!\,(x_B N)!]$$

When the number of sites N is very large, as is the case in a mole of a mineral, we can simplify this expression by using Stirling's approximation:

$$\ln N! = N \ln N - N$$

Thus $$S = -Nk(x_A \ln x_A + x_B \ln x_B)$$

For a mole of sites N is Avogadro's number (6.02×10^{23} mol^{-1}) and $Nk = R$, the gas constant (8.31 J mol^{-1}K^{-1}).

Hence $$S = -R(x_A \ln x_A + x_B \ln x_B)$$

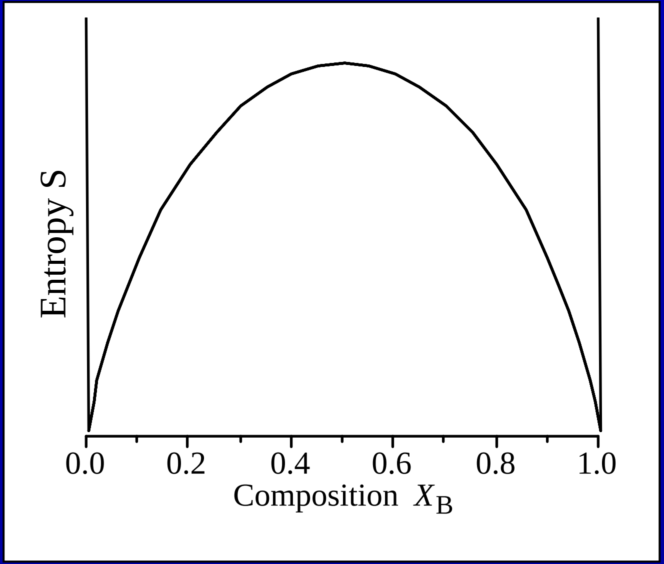
In a complex mineral structure there may be more than one site per formula unit over which disorder can occur and the more general form of the above expression is

$$S = -nR(x_A \ln x_A + x_B \ln x_B)$$

where n is the number of sites on which mixing occurs

This expression is known as the *entropy of mixing*.

Since x_A and x_B are both fractions, S is always positive as shown below, which gives the general form of the curve for the entropy of mixing ΔS as a function of the atomic fraction x_B of B atoms.



Example 2 Entropy of mixing Fe and Mg over the M1 and M2 sites in olivine $(Mg,Fe)_2SiO_4$

$$S = -nR(x_A \ln x_A + x_B \ln x_B)$$

For a composition 50 mole% forsterite (Mg_2SiO_4) and 50 mole% fayalite (Fe_2SiO_4) :

$$S = -nR(x_A \ln x_A + x_B \ln x_B)$$ (Note: n=2 for olivine because there are 2 sites for mixing in each formula unit)

$$= -2R(0.5 \ln 0.5 + 0.5 \ln 0.5)$$

$$= 11.52 \text{ J mol}^{-1} \text{ K}^{-1}$$

For a composition 25 mole% forsterite (Mg_2SiO_4) and 75 mole% fayalite (Fe_2SiO_4) :

$$S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$= -2R(0.25 \ln 0.25 + 0.75 \ln 0.75)$$

$$= 9.34 \text{ J mol}^{-1} \text{ K}^{-1}$$

Vibrational entropy

- the entropy associated with lattice vibrations

Energy of lattice vibrations is quantised - each quantum of vibrational energy is a *phonon.*

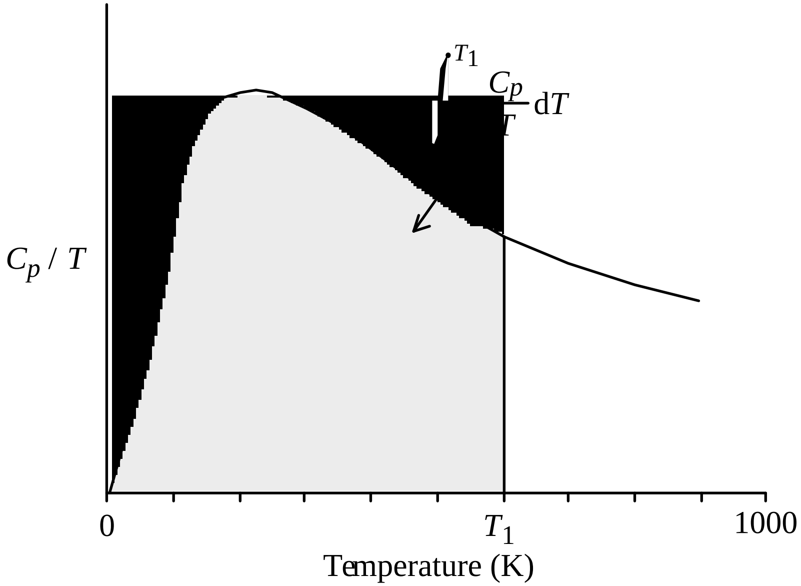
Increasing the amplitude of atomic vibrations increases the number of phonons. The phonon spectrum defines the number of phonons in each frequency range : the phonon density of states.

Vibrational entropy arises from the number of ways of distributing phonons over the vibrational energy levels in a crystal.

Vibrational entropy *S* is related to the heat capacity C_p :

For a reversible process $dS = dQ/T$ and since $C_p = dQ/dT$ $dS/dT = C_p/T$ and

$$S = \int \frac{C_P}{T} dT \qquad S = S_0 + \int_0^{T_1} \frac{C_P}{T} dT$$



The Gibbs free energy, *G*, and equilibrium

Example: the transformation of aragonite to calcite:

aragonite ⇒ calcite

ΔH^o = +370 Joules at 25°C and 1 atm.

The entropy of aragonite and calcite under the same conditions is 88 J mol^{-1} K^{-1} and 91.7 J mol^{-1} K^{-1} respectively. Thus for the transformation

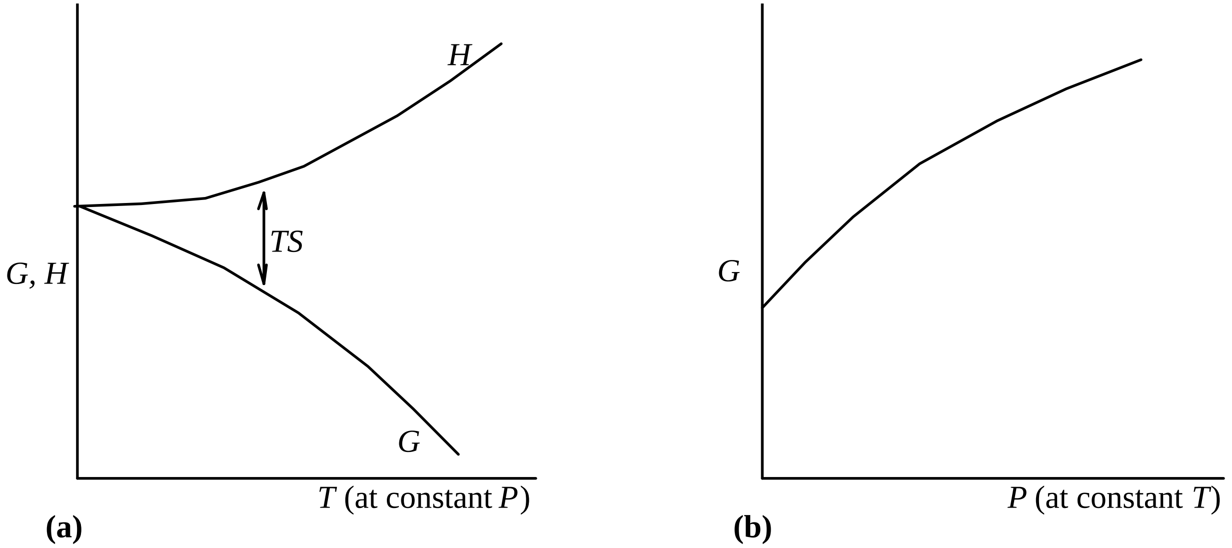
aragonite ⇒ calcite

ΔS^o = +3.7 J mol^{-1} K^{-1} at 25°C and 1 atm.

Therefore ΔG for the aragonite ⇒ calcite transformation equals $\Delta H - T\Delta S$ = +370 - (298 x 3.7) = -732.6 Joules.

Calcite thus has the lower free energy and is the stable polymorph of calcium carbonate at 25°C and 1 atm. pressure.

Variation of enthalpy and free energy as a function of T and P



We can derive the relations between G, T and P from the basic definitions of the thermodynamic functions as follows:

$$G = H - TS$$

Substituting $H = U + PV$ into this equation gives

$$G = U + PV - TS$$

Differentiating gives

$$\mathrm{d}G = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T.$$

From the first law, $\mathrm{d}U = \mathrm{d}Q - P\mathrm{d}V$, and for a reversible process (which is always in equilibrium) $\mathrm{d}Q = T\mathrm{d}S$.

On substitution

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \qquad \text{at equilibrium}$$

Therefore at constant pressure:

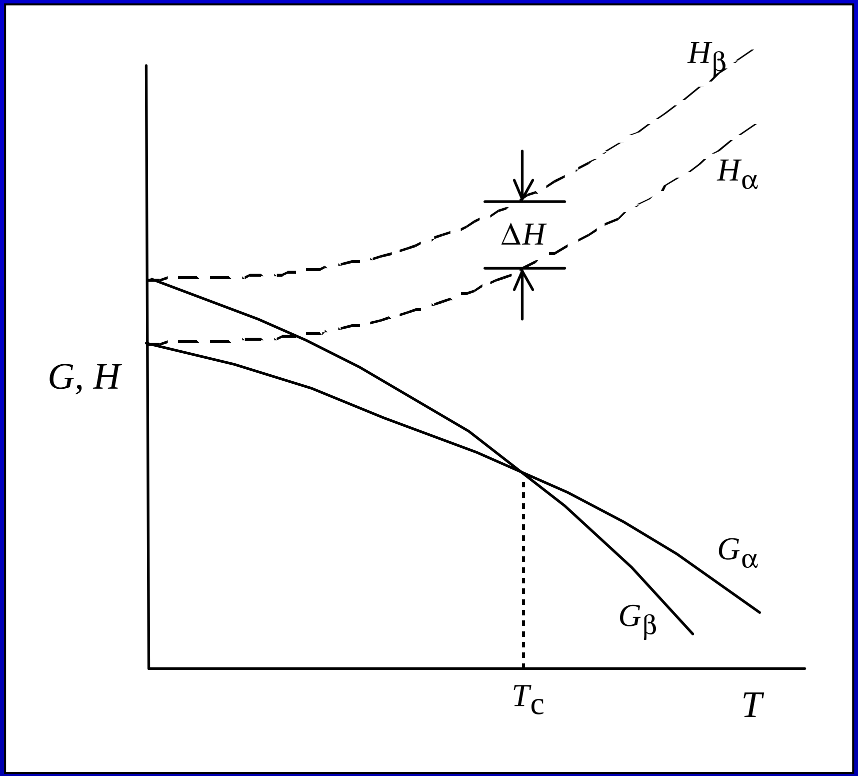
$$(\partial G/\partial T)_p = -S$$

and at constant temperature:

$$(\partial G/\partial P)_T = V$$

The figure in the previous slide shows the way in which the free energy of a mineral structure changes when it maintains equilibrium with a changing T and P.

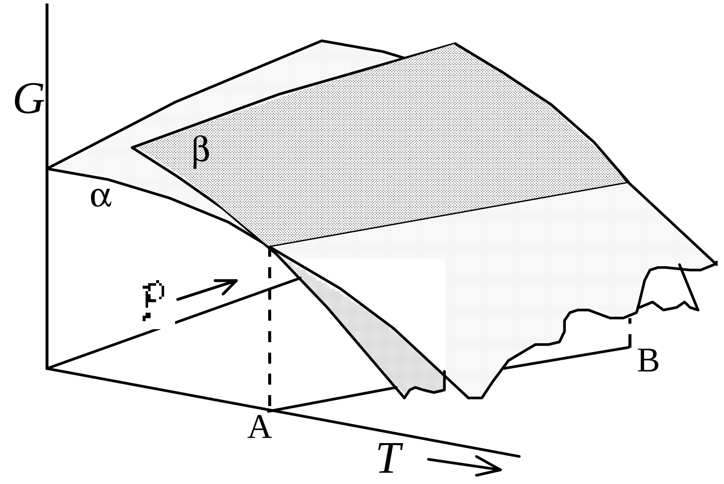
For a polymorphic transformation:



The figure shows the free energy and enthalpy curves for two phases α and β as a function of T

Above T_c the β phase is more stable than the α phase (it has a lower free energy). The enthalpy change at T_c is called the latent heat of transformation (ΔH)

If we consider both temperature and pressure stability fields for two polymorphs α and β, the free energy curves become surfaces in *G–T–P* space and their intersection defines the equilibrium between α and β.



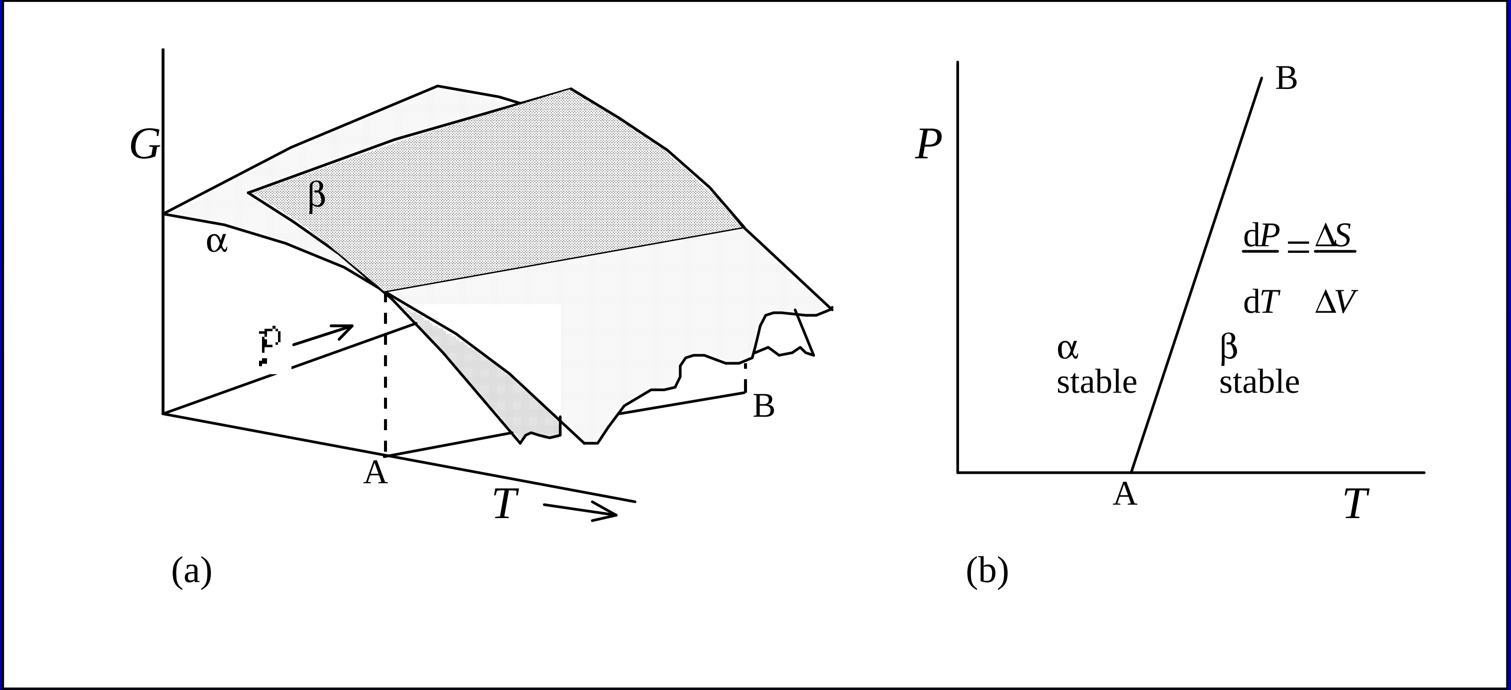
(a)

The slope of this intersection line when projected on the *P*–*T* plane, i.e. d*P*/d*T* is given by the *Clapeyron relation* which arises from the equilibrium relation ΔG = 0. At equilibrium,

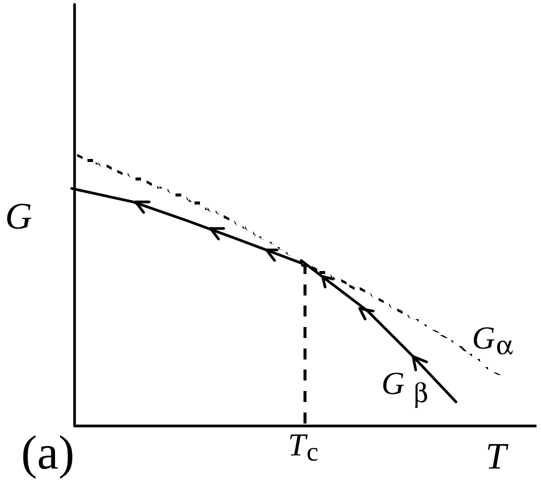
$$\Delta V \mathrm{d}P = \Delta S \mathrm{d}T$$

and hence

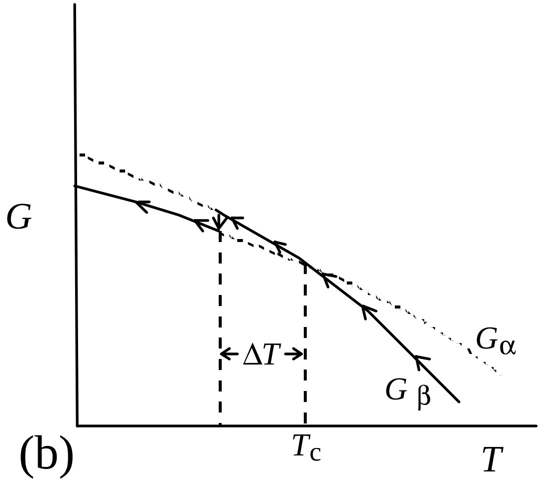
$$\mathrm{d}P/\mathrm{d}T = \Delta S/\Delta V$$



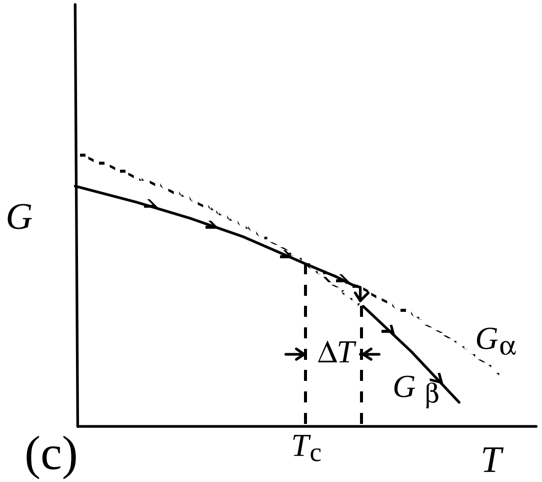
Reversible and irreversible processes. Metastability



Reversible at T_c



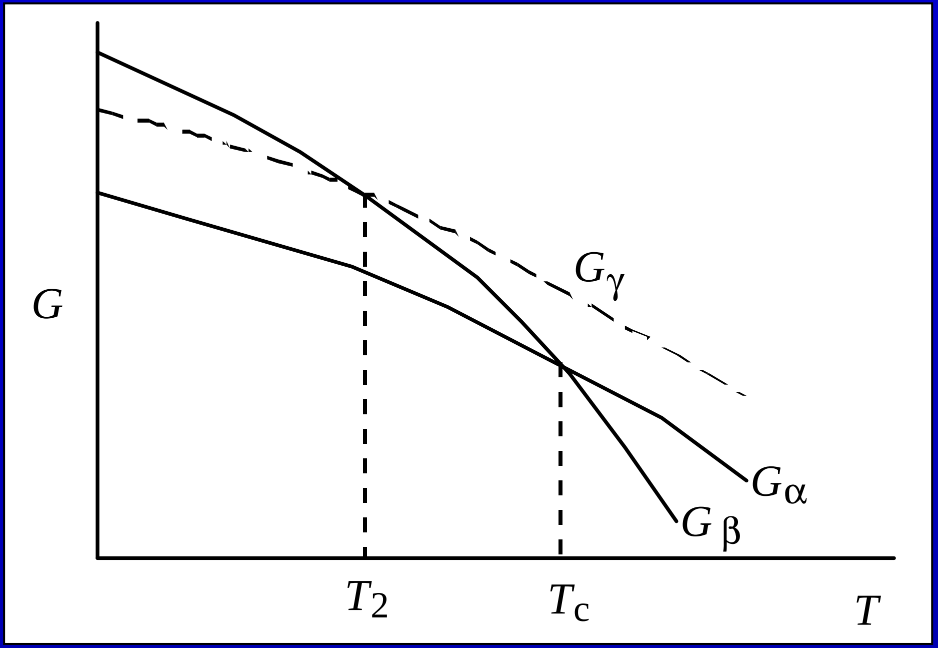
Large undercooling



Smaller superheating

Case (a) is never observed in practice because at T_c (equilibrium) the free energy of both phases is the same. Undercooling (case b) is always required to produce a free energy ‘drive’ for the transition from α to β. During heating the overheating is generally less.

Reversible and irreversible processes. Metastability

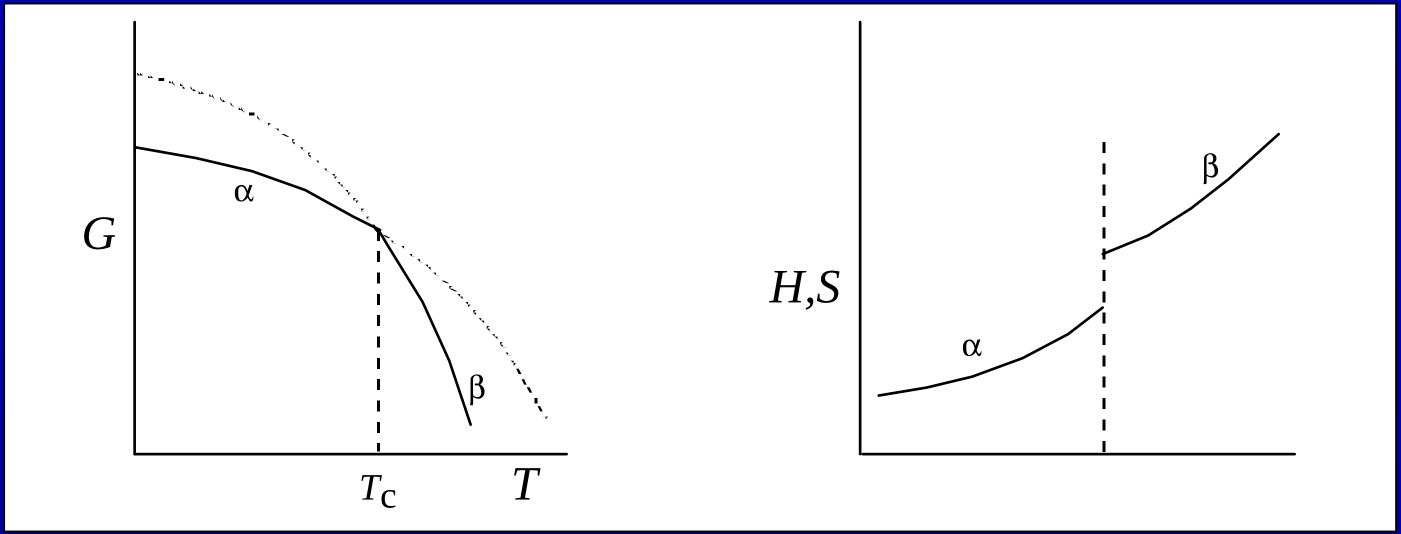


As phase β is cooled from high T it should transform to phase α below T_c. If the transition is kinetically impeded, then phase α could persist to temperature T_2. In that case a transition to the metastable phase γ can occur. This is the case in the case of high tridymite (β) transforming to low tridymite (γ). Phase α would be high quartz.

First- and second-order phase transitions

At the equilibrium temperature (or pressure), the free energies of the two polymorphs are equal, and there is no discontinuity in the free energy *G* on passing from one structure to another.

In *first-order phase transitions* the first derivatives of the free energy $\partial G/\partial T$ and $\partial G/\partial P$ are discontinuous. Since $\partial G/\partial T = -S$ and $\partial G/\partial P = V$, first order phase transitions are characterized by discontinuous changes in entropy and volume at the critical temperature.

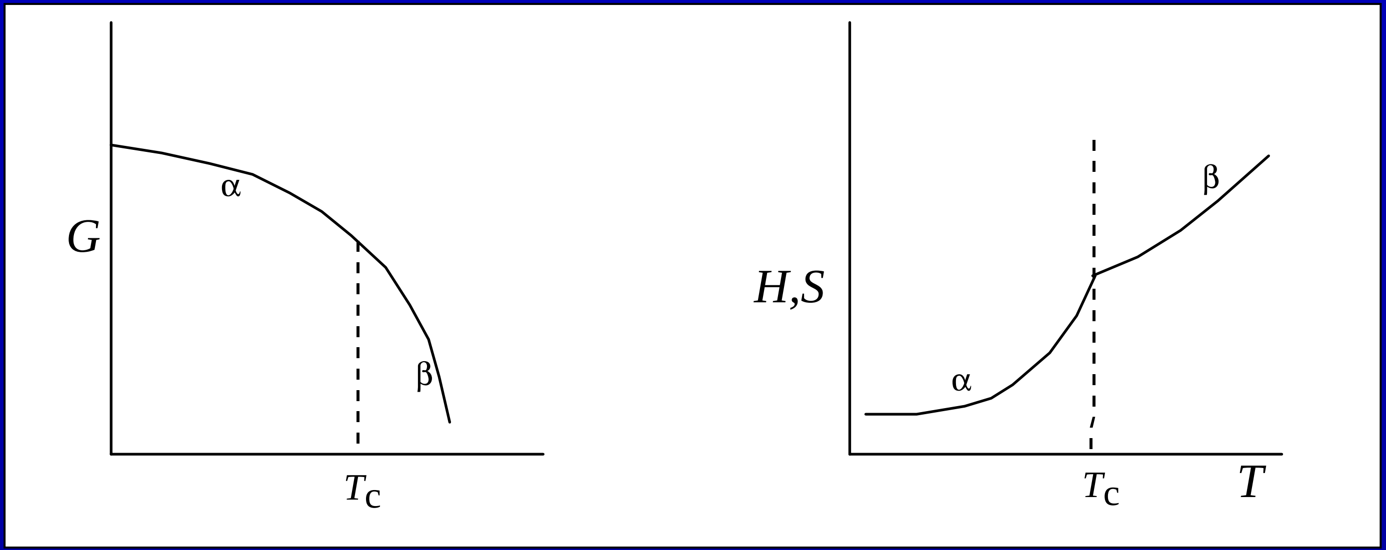


In *second-order phase transitions* the first derivatives of the free energy are continuous, but the second derivatives $\partial^2 G/\partial T^2$ and $\partial^2 G/\partial P^2$ are discontinuous. The enthalpy change is continuous and so there is no latent heat associated with second order transitions. Since

$$\partial^2 G/\partial T^2 = - \partial S/\partial T = - C_p/T$$

and $$\partial^2 G/\partial P^2 = - V\beta \; ; \qquad \partial^2 G/\partial T \partial P = V\alpha$$

the discontinuities occur in the specific heat capacity C_p , the compressibility β and the thermal expansion α.



Although the thermodynamic classification of a phase transition cannot be simply related to a transformation mechanism, we can say that:

First order phase transitions are generally reconstructive transitions

e.g. quartz ⇔ tridymite ⇔ cristobalite

Second order phase transitions are generally displacive transitions

e.g. high quartz ⇔ low quartz