V - High pressure methods

Geophysics and geochemistry have given a strong impetus to the study of physical properties or to the synthesis of materials at high pressure. Polymorphic phase transformations, chemical mixing by coupled diffusion-convection play a key role in the upper and deep earth's mantle evolution. The design of high pressure autoclaves (0.5 GPa-1500 °C) and, latter, of multi anvil or diamond press (400 GPa-5000 K by laser heating), coupled with in situ physical characterisations (Raman, X-ray diffraction...), has opened immense new fields of investigation. Moreover, materials unknown in nature are now synthesised at high temperature and high pressure ; they can be quenched in their metastable state.

1. Metastability and phase boundaries

Large changes in the density, electronic state and free energy accompany the pressure increase. For example, alkali metals undergo the electronic transition $ns^1 \rightarrow (n\text{-}1)d^1$; caesium at 15 GPa is four times denser that at atmospheric pressure and superconducts.

The variations of the Gibbs energy for caesium metal as a function of temperature and pressure are compared in figure 24. The opposite effects clearly show that pressure favours metastable phases while temperature transforms metastable phases to thermodynamically stable phases.

The influence of pressure was already evidenced in the P-T diagram of water (figure 12.2) : metastable phases appear at high pressure (ice V, ice VI ...). Their melting temperature increases with pressure (the inverse anomalous effect, observed at P<200 MPa, is due to hydrogen bonding).

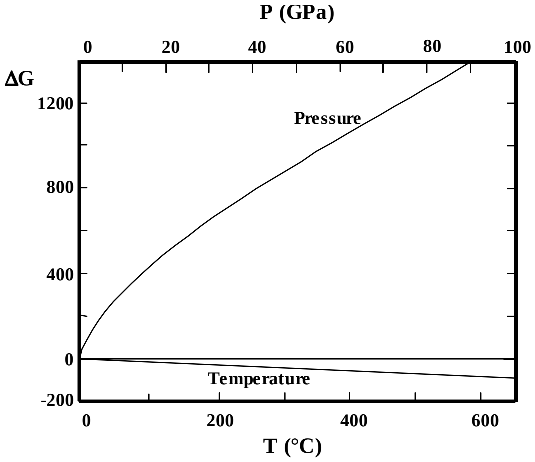

Figure 24. Comparison of the Gibbs energy variation of caesium with pressure and temperature.

The evolution of the transition temperature with pressure is related to the entropy variation and to the volume change (Clapeyron equation) : at the equilibrium between α and β phases, the chemical potentials must remain equal in α and β when infinitesimal changes in temperature and pressure occur. Gibbs-Duheim relation ($d\mu = -SdT + VdP$) gives the chemical potential for T and P variables (see Box 1) :

$$d\mu_\alpha = -S_\alpha dT + V_\alpha dP = d\mu_\beta = -S_\beta dT + V_\beta dP \;\Rightarrow\; (V_\beta - V_\alpha)dP = (S_\beta - S_\alpha)dT\ .$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{(Clapeyron equation).} \qquad \{19\}$$

ΔS and ΔV, known at a reference p* pressure and T* temperature, represent the entropy and the volume changes at the transition $\alpha \rightarrow \beta$.

Solid state transitions, together with solid-liquid, liquid-vapour, solid-vapour transformations obey this relation. Therefore, the Clapeyron equation transforms to :

$$\text{solid-liquid} \qquad \frac{dP}{dT} = \frac{\Delta H_m}{T\Delta V_m} \text{ and } p = p^* + \frac{\Delta H_m}{\Delta V_m} \mathrm{Log}\frac{T}{T^*} \qquad \{20\}$$

liquid-vapour $$\frac{d\mathrm{Log}\,P}{dT} = \frac{\Delta H_v}{RT^2}$$ (Clausius-Clapeyron equation) {21}

for a perfect gas ($\Delta V = \frac{RT}{P}$) : $$p = p^* \exp\left[\frac{-\Delta H_v}{R}\left(\frac{1}{T} - \frac{1}{T*}\right)\right]$$ {22}

Good estimates of water vapour pressure between 100°C and the critical point (see Box 4) are obtained with $\Delta H_v = 40.66\ \mathrm{kJ\ mol^{-1}}$. The pressures, in the temperature range of zeolite synthesis, are :

T(°C)	140	160	180	200	220	240
P(10^5 Pa)	3.0	5.2	8.5	13.5	20.5	30.2

(The reference pressure and temperature (p* and T*) are taken at the critical point).

2. High pressure synthesis and high pressure transformations

The most famous industrial synthesis at high pressure and high temperature certainly concerns diamond. More than 100 million carats (20 tons) a year are produced world-wide. Small crystals are obtained (at best one millimetre in size) and are used for cutting tools or abrasive manufacture.

Diamond (cubic, F, a=3.56Å, Z=8) is metastable at room temperature (ΔG=-2.90 kJ mol^{-1}). Diamond density is 3.538, as compared to 2.282 for graphite (hexagonal, a=2.546 Å, c=6.696 Å, Z=4). Consequently, the transformation $C_g \rightarrow C_d$ under pressure is theoretically possible (figure 12.25) ; however, it is kinetically impossible : carbon-carbon bonds must be broken in a flux.

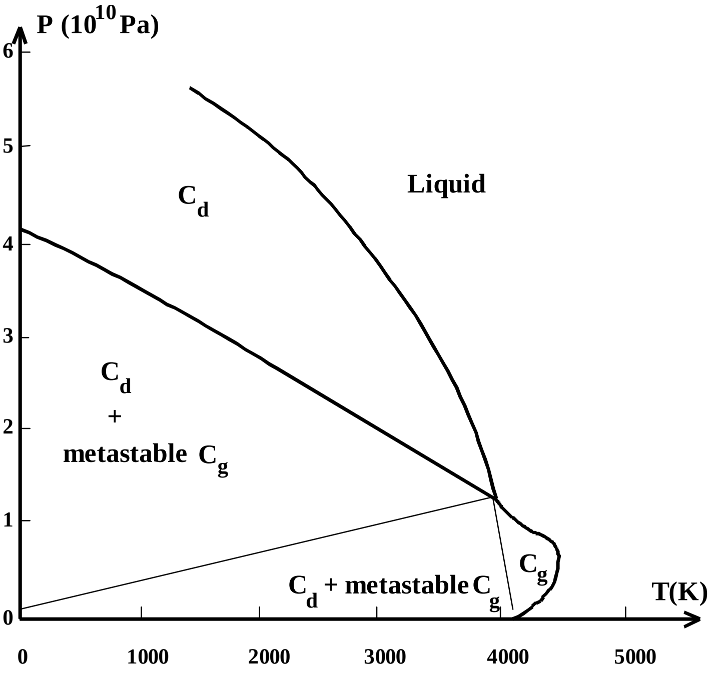

Figure 25. - (P,T) phase diagram of carbon.

Molten d-metals are convenient for this purpose and diamond can be grown at 7 GPa from the BA liquidus (1455°C - 1394°C) of the nickel-carbon diagram shown in figure 26. Typical experimental conditions are : growth rate ≈1 mm/day, Fe-Co-Ni flux, "Belt" tetrahedral press or octahedral multianvil cell (figure 12.27a). The sample (graphite) is inserted in a gasket of ceramic or $AlSi_2O_5(OH)$ pyrophillite. These materials extrude slightly between the tungsten carbide pistons of the press and act as a sealed container. The growth of diamond gems is possible but too costly (H.T. Hall at General Electric, US in 1955).

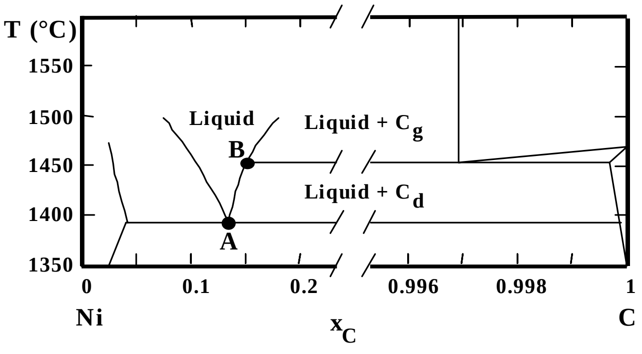

Figure 26. - Ni-C phase diagram.

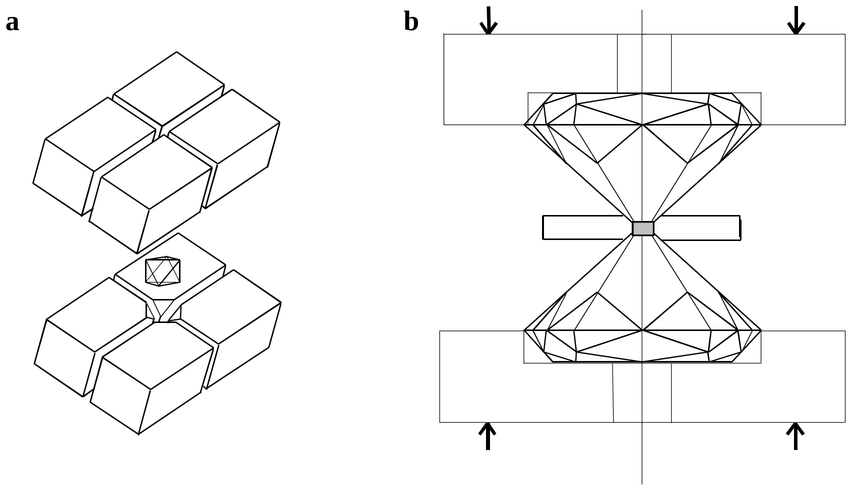

Figure 27. - Octahedral multianvil (a) and diamond (b) pressure cells.

Very high pressures can be obtained in "simple" diamond anvil cells (figure 27b). Two opposed diamonds with rigorously parallel faces are loaded with a nutcracker type device. They compress a metallic film drilled with a hole where the sample (liquid, solid, gas) is inserted. Small ruby crystals are added for pressure measurement (red shift of the R_1-R_2 fluorescence doublets). Laser heating and spectroscopic or X-ray characterisation of the sample are performed through the transparent diamond windows.

Numerous transitions, representative of the mineral transformations in the earth's mantle, have been studied :

$(Mg,Fe)_2SiO_4$ olivine → $(Mg,Fe)_2SiO_4$ spinel (1200 °C, 3.3 GPa)

(zone mantle from 400 to 700 km depth)

$Ca(Mg,Fe)Si_2O_6$ pyroxene → $(Mg,Fe)SiO_3 + CaSiO_3$ perovskite (2000 °C, 20 GPa)

(zone mantle around 1000 km depth)

The influence of a pressure increase is generally :

- the increase of the melting or transformation temperatures ; the melting temperature of NaCl is 1550 °C at 6.5 GPa (800 °C at atmospheric pressure); $MgCO_3$ magnesite is stable at 2000 °C, 30 GPa.
- the stabilisation of high coordination numbers ; silicon adopts the octahedral coordination in $CaSiO_3$ perovskite (1800 °C, 20 GPa) or stishovite SiO_2 (rutile type, T=1200 °C, P=12 GPa). $KAlSi_3O_8$ sanidine transforms into the hollandite type structure (Al and Si in octahedral coordination) at T=900 °C and P=12 GPa.
- the stabilisation of unusual oxidation states ; perovskites with Cr^{IV}, Ni^{III}, Cu^{III} have been prepared under oxygen pressure : $SrCrO_3$, $LnNiO_3$ (Ln=rare-earth). Numerous copper oxides, related to the High T_C superconductors, are also synthesised under medium or high oxygen pressure : $LaCuO_3$