

# Pressure dependence

## Equilibrium constant

We can see from the gas phase form of the equilibrium constant that the equilibrium concentrations of species depend on pressure. This dependence is “inside” the equilibrium constant. The equilibrium constant is not changed but the individual species are affected for a given value of  $K$  at  $P_{\text{tot}}$ , the total pressure.

## Gibbs free energy

The pressure dependence of free energy contained in the the term  $dG = VdP$  is a different dependence, which can result in a shift in the equilibrium constant itself.

# Pressure dependence of species at equilibrium

We can see from the gas phase form of the equilibrium constant that pressure of species depend on pressure. For the general gas phase reaction,



we can write the equilibrium constant as

$$K = \frac{P_Z^z}{P_C^c P_D^d}$$

And the free energy is

$$\Delta G^\circ = -RT \ln \frac{P_Z^z}{P_C^c P_D^d}$$

From Dalton's law

$$P_C = x_C P_{tot}, P_D = x_D P_{tot}, P_Z = x_Z P_{tot}$$

# Pressure dependence of species

If we substitute these mole fractions and total pressure into the equilibrium constant we have

$$\Delta G^{\circ} = -RT \ln \frac{x_Z^z}{x_C^c x_D^d} P_{tot}^{z-c-d}$$

Which depends on the total pressure unless  $z - c - d = 0$ .

This expression shows that, in general, the free energy depends on the total pressure. This means that for the fixed pressure may affect the proportion of products to reactants.

# The variation of the Gibbs energy with pressure

We have shown that  $dG = VdP - SdT$ . This differential can be used to determine both the pressure and temperature dependence of the free energy. At constant temperature:  $SdT = 0$  and  $dG = VdP$ .

The integrated form of this equation is:

$$\Delta G = \int_{P_1}^{P_2} VdP$$

For one mole of an ideal gas we have:

$$\Delta G_m = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \left( \frac{P_2}{P_1} \right)$$

Note that we have expressed  $G$  as a molar quantity  $G_m = G/n$ .

# The variation of the Gibbs energy with pressure

We can use the above expression to indicate the free energy at some pressure  $P$  relative to the pressure of the standard state  $P = 1 \text{ bar}$ .

$$G_m(T) = G^0(T) + RT \ln \left( \frac{P}{1 \text{ bar}} \right)$$

$G^0(T)$  is the standard molar Gibbs free energy for a gas. As discussed above the standard molar Gibbs free energy is the free energy of one mole of the gas at 1 bar of pressure. The Gibbs free energy increases logarithmically with pressure. This is entirely an entropic effect.

Note that the 1 bar can be omitted since we can write:

$$RT \ln \left( \frac{P}{1 \text{ bar}} \right) = RT \ln (P) - RT \ln (1) = RT \ln (P)$$

# Pressure dependence of the free energy for liquids and solids

When considering the equilibrium between liquids and solids the molar volume change between the two phases enters into the pressure dependence as:

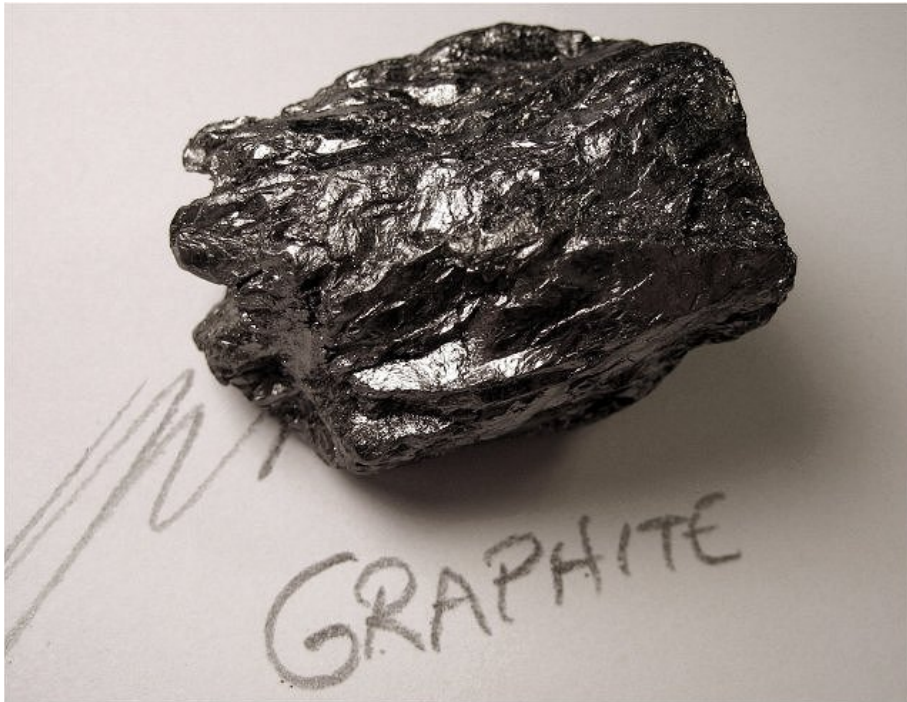
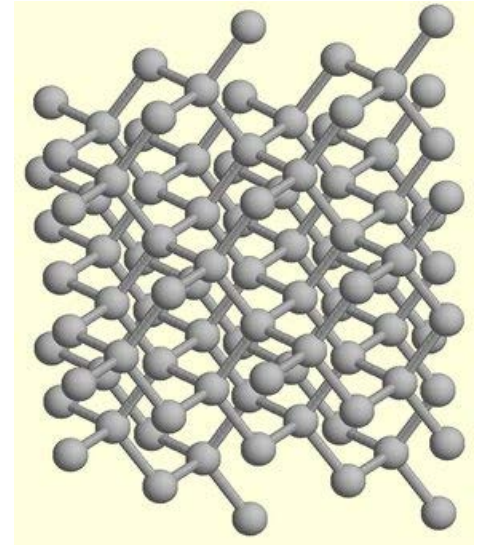
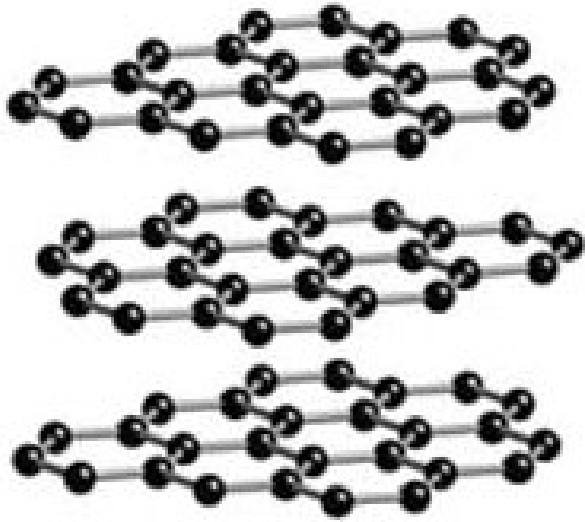
$$\Delta G(P) = \Delta G^0 + \Delta V_m(P - 1)$$

The molar volume can be calculated from density data as follows:

$$V_m = \frac{M}{\rho}$$

where  $M$  is the molar mass. Therefore, the molar volume change is:

$$\Delta V_m = \frac{M}{\rho_2} - \frac{M}{\rho_1}$$



diamond

# Shift in equilibrium due to pressure: the formation of diamond

Graphite and diamond are two forms of carbon. Given that the free energy of formation of diamond is:



and the densities are:

$$\rho(\text{graphite}) = 2.26 \text{ and } \rho(\text{diamond}) = 3.51$$

calculate the pressure required to transform carbon into diamond.



# Shift in equilibrium due to pressure: the formation of diamond

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calculate the pressure required to transform carbon into diamond.

Solution: Graphite will be in equilibrium with diamond when:

$$0 = \Delta G^\circ + \Delta V_m (P - 1)$$
$$P = 1 - \frac{\Delta G^\circ}{\Delta V_m} = 1 - \frac{\Delta G^\circ}{\frac{M}{\rho_d} - \frac{M}{\rho_{gr}}}$$

# Example: the formation of diamond

Plugging the values we find:

$$0 = \Delta G^0 + \Delta V_m(P - 1)$$

$$P = 1 - \frac{\Delta G^0}{\Delta V_m}$$

$$\Delta V_m = \frac{0.012 \text{ kg/mole}}{3510 \text{ kg/m}^3} - \frac{0.012 \text{ kg/mole}}{2260 \text{ kg/m}^3} = -1.89 \times 10^{-6} \frac{\text{m}^3}{\text{mole}}$$

$$P = 1 - \frac{2900 \text{ Joules/mole}}{-1.89 \times 10^{-6} \frac{\text{m}^3}{\text{mole}}} = 1.5 \times 10^9 \text{ Pa}$$
$$= 15,000 \text{ bars}$$

# Exploring the significance

When  $\Delta G = 0$  graphite and diamond are in equilibrium. That implies that the amounts of reactants and products are equal. These conditions would not be very appropriate for industrial production of diamond since the diamond would be  $\frac{1}{2}$  graphite! If we want a diamond sample that is 99.9% pure then the reaction quotient  $Q = 1000$ . In this case, we could calculate the effective driving force ( $\Delta G$ ) required.

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G = 2,900 \frac{\text{J}}{\text{mol}} + 2,470 \frac{\text{J}}{\text{mol}} \ln (1000)$$

$$\Delta G = 19,960 \frac{\text{J}}{\text{mol}}$$

# Industrial diamond production

Thus, for a more realistic condition required to produce diamond we have:

$$\Delta G = \Delta G^0 + \Delta V_m (P - 1)$$

$$P = 1 - \frac{\Delta G - \Delta G^0}{\Delta V_m}$$

$$\begin{aligned} P &= 1 - \frac{17,000 \text{ Joules/mole}}{-1.89 \times 10^{-6} \frac{\text{m}^3}{\text{mole}}} = 9 \times 10^9 \text{ Pa} \\ &= 90,000 \text{ bars} \end{aligned}$$