3.1 The principle of Le Chatelier

In this section we will discuss consequences of Le Chatelier‘s principle:
When subjected to an external influence the state of the system at equilibrium shifts in that direction which tends to nullify the effect of the external influence.
Typical external effects which may induce a shift in equilibrium are pressure, temperature, but also e. g. applying external electrical potentials to an electrochemical system.
The starting point for this discussion is the fundamental equation for thermodynamic equilibrium

$$dG = Vdp - SdT + \sum_j \mu_j dn_j = 0 \quad . \tag{3.1}$$

Taking mechanical and thermal equilibrium, i.e. $dp = dT = 0$, we get

$$dG_{p,T} = \sum_j \mu_j dn_j = 0 \quad . \tag{3.2}$$

Introducing the extent of reaction ξ, e.g. for $A \leftrightarrow B$,

$$d\xi = \frac{dn_B}{\nu_B} = dn_B = \frac{dn_A}{\nu_A} = -dn_A \quad , \tag{3.3}$$

we finally get

$$dG_{p,T} = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi \quad , \tag{3.4}$$

leading to the definition of a reaction energy

$$\Delta_r G = \frac{dG_{p,T}}{d\xi} = \mu_B - \mu_A \quad . \tag{3.5}$$

This equation is the fundamental justification for the name ”chemical potential” because the difference of chemical potentials is the driving force for chemical reactions (which can be directly extracted from the slope of the Gibbs potential vs. the extent of reaction ξ).

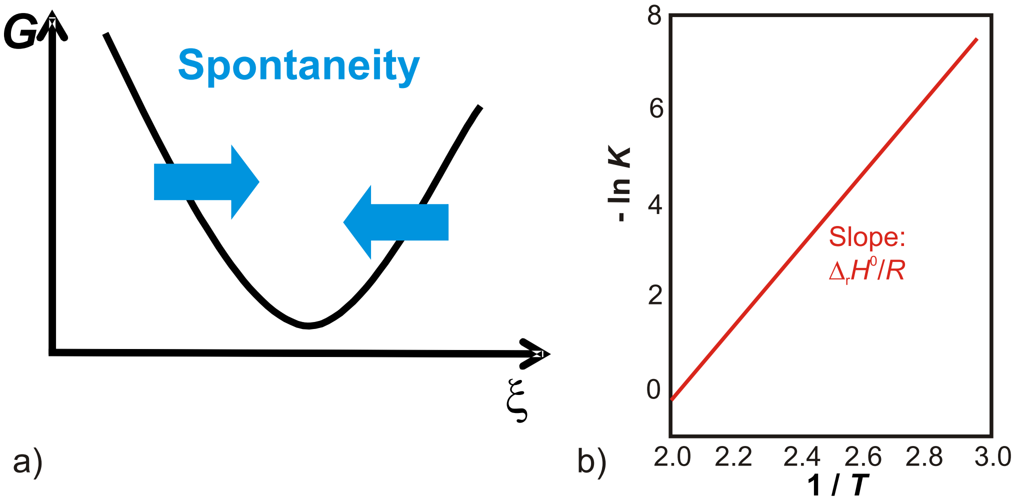

Figure 3.1: a) Gibbs potential and spontaneous reactions. b) Plot according to Eq. (3.13).

As illustrated in Fig. 3.1 a) we distinguish three cases:

- Equilibrium condition: $\Delta_r G = 0$
- Exergonic, spontaneous for the forward reaction: $\Delta_r G < 0$
- Endergonic, spontaneous for the reverse reaction: $\Delta_r G > 0$

In the general case we have

$$dG_{p,T} = \sum_j \mu_j dn_j = \sum_j \mu_j \nu_j d\xi \quad \Rightarrow \quad \Delta_r G = \left(\frac{dG}{d\xi}\right)_{p,T} = \sum_j \mu_j \nu_j \quad , \tag{3.6}$$

leading to

$$\Delta_r G = \sum_j \left(\mu_j^0 + RT \ln \frac{p_j}{p^0}\right) \nu_j = \Delta_r G^0 + RT \ln \prod_j \left(\frac{p_j}{p^0}\right)^{\nu_j} \quad \text{or} \quad \Delta_r G = \Delta_r G^0 + RT \ln \prod \frac{\left(\frac{p_{pr}}{p^0}\right)^{|\nu^{prod}|}}{\left(\frac{p_{ed}}{p^0}\right)^{|\nu^{ed}|}} \quad . \tag{3.7}$$

In equilibrium $\Delta_r G = 0$, i.e.

$$\Delta_r G^0 = -RT \ln \prod \frac{\left(\frac{p_{pr}}{p^0}\right)^{|\nu^{prod}|}}{\left(\frac{p_{ed}}{p^0}\right)^{|\nu^{ed}|}} = -RT \ln K_p \quad \text{or} \quad K_p = \prod \frac{\left(\frac{p_{pr}}{p^0}\right)^{|\nu^{prod}|}}{\left(\frac{p_{ed}}{p^0}\right)^{|\nu^{ed}|}} = \prod_i \left(\frac{p_i}{p^0}\right)^{\nu_i} \quad , \tag{3.8}$$

which is one version of the famous mass action law where K_p is the equilibrium constant for pressures. Correspondingly we define

$$K_x := \prod_i x_i^{\nu_i} \quad . \text{ Since } \quad x_i = \frac{p_i}{p_{tot}} \quad \Rightarrow \quad \ln(K_p) = \ln(K_x) + \sum_i \ln \left(\frac{p_{tot}}{p^0}\right)^{\nu_i} \quad , \tag{3.9}$$

we get a second representation of the mass action law for concentrations.
The principle of Le Chatelier now tells how K (resp. $\ln K$ or $\Delta_r G^0$) and thus equilibrium concentration (resp. activities) or partial pressure (resp. fugacity) change on external effects. Examples are

- cooling favors the heat producing reaction: $2\mathrm{NO}_2 = \mathrm{N}_2\mathrm{O}_4 - \Delta H$.
- applying pressure to gases favors reaction with less particles produced.
- more complex scenarios may combine both effects: High $T \rightarrow \quad \mathrm{N}_2 + 3\mathrm{H}_2 = 2\mathrm{NH}_3 - \Delta H \quad \leftarrow$ High p

  A high temperature is needed for the activation of N_2, but the consequently occurring increase of p is critical for the processes. Workarounds can be A) Use of catalysts or B) Removal of products.