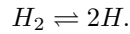


# Example of a chemical reaction $H_2 \rightleftharpoons 2H$

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We consider the following reaction



Where the  $H_2$  molecules have energy  $-\epsilon$  and the  $H$  atoms have zero energy. We initially have only  $H_2$  molecules,  $N_{H_2,i} = N$ ,  $N_{H,i} = 0$ . As a function of the number of reactions,  $R$ , the number of each type of substance is given by

$$N_{H_2} = N - R \quad N_H = 2R,$$

and thus

$$2N_{H_2} + N_H = \text{const} = 2N.$$

The reaction constant is given by

$$K_p(T) = \exp(-\beta(\chi_{H_2}(T) - 2\chi_H(T)))$$

where

$$\begin{aligned}\chi_H(T) &= 3 \ln \lambda_{T,H} - T \ln T \\ \chi_{H_2}(T) &= 3T \ln \lambda_{T,H_2} - \epsilon - T \ln T = 3 \ln \lambda_{T,H} - T \ln \sqrt{8} - \epsilon - T \ln T.\end{aligned}$$

We thus obtain

$$K_p(T) = \exp(3 \ln \lambda_{T,H} - \ln T + \ln \sqrt{8} + \beta\epsilon) = \frac{\lambda_{T,H}^3}{T} e^{\beta\epsilon}.$$

According to the law mass action we obtain

$$\frac{c_{H_2}}{c_H^2} = \frac{N_{H_2}(N_{H_2} + N_H)}{N_H^2} = PK_p(T) = \frac{P\lambda_{T,H}^3}{T} e^{\beta\epsilon} \equiv \alpha$$

Note that I did not replace  $P$  with  $(N_{H_2} + N_H)T/V$  as I demonstrated in class since  $V$  is not constant. Nevertheless, is the assumption of ideal gas is justified the clearly  $P\lambda_{T,H}^3/T \ll 1$ . We now have to equations to solve

$$\begin{aligned}2N_{H_2} + N_H &= 2N \\ \frac{N_{H_2}(N_{H_2} + N_H)}{N_H^2} &= \alpha\end{aligned}$$

The solution is given by

$$\frac{(N - \frac{1}{2}N_H)(N + \frac{1}{2}N_H)}{N_H^2} = \alpha$$
$$N^2 - \frac{1}{4}N_H^2 = \alpha N_H^2$$
$$N_H = \frac{N}{\sqrt{\alpha + \frac{1}{4}}}$$

- In the limit of  $T \sim \epsilon$  or higher,  $e^{\beta\epsilon} \sim O(1)$  and thus  $\alpha \ll 1$ . Therefore for high temperatures we obtain that  $N_H = 2N$ , i.e. all the hydrogen molecules dissociated to the state which is entropically preferable.
- In the limit of  $T \ll \epsilon$ , we obtain  $\alpha \gg 1$ . Therefore for low temperatures we obtain that  $N_H = 0$ , implying that the hydrogen molecules remained in the energetically preferable state.