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

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We consider the following reaction

$$H_2 \rightleftharpoons 2H.$$

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

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

and thus

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

The reaction constant is given by

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

where

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

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

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

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 disocciated 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.