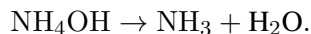


1. A chemical decomposition.

Consider the decomposition of ammonium hydroxide into ammonia and water:



We call the decomposition of the ammonium hydroxide the “forward reaction”. For this problem, you will assume that the “backward reaction,” the generation of ammonium hydroxide from ammonia and water, is negligible. We will use $p(t)$ to denote the probability that a single ammonium hydroxide molecule has not yet decomposed after a time t , and we will use $[\text{NH}_4\text{OH}]$, $[\text{NH}_3]$, and $[\text{H}_2\text{O}]$ to denote the concentrations of the three chemical species.

(i) Imagine recording the fate of a single ammonium hydroxide molecule every Δt units of time. If at the beginning of the Δt time interval the molecule is intact, the probability of decomposing by the end of the time interval is given by α . What is $p(n\Delta t)$, the probability that the initial ammonium hydroxide molecule has not decomposed at time $t = n\Delta t$ after an integer number n of such Δt intervals? Express your answer in terms of n and α .

[Hint: You can (and should) assume that the behavior during one interval Δt does not impact the probability of decomposition in the other intervals of time.]

(ii) As the time interval Δt is made smaller, α will also decrease. We define

$$k_f = \lim_{\Delta t \rightarrow 0} \frac{\alpha}{\Delta t},$$

which is the probability per unit time of a molecular decomposition in an infinitesimal time interval. By taking the $\Delta t \rightarrow 0$ limit of your answer to (i), express $p(t)$ in terms of k_f and t .

[Hint: $e^x = \lim_{n \rightarrow \infty} \left(1 + \frac{x}{n}\right)^n$.]

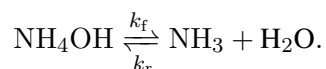
(iii) Use your answer to (ii) to derive an expression for $dp(t)/dt$ in terms of k_f and $p(t)$. In the event that you could not figure out (ii), I will award partial credit if you are able to write down the correct expression by intuition or by working backwards from (iv).

(iv) Assume you start with N ammonium hydroxide molecules in a volume V . Relate $p(t)$ to $[\text{NH}_4\text{OH}](t)$ and use (iii) to derive the rate of decay of the NH_4OH concentration:

$$\frac{d[\text{NH}_4\text{OH}]}{dt} = \dots$$

(v) Our procedure in this problem appears to be quite generic. We’ve said nothing about the chemical mechanism of decomposition, only that the probability of decomposing in time Δt is α . Why then could some molecules actually decompose with a decay probability different than the one you found in (ii)? (I’m looking for something more than the fact that we have neglected the backward reaction.)

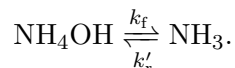
2. **Dynamic equilibrium.** Now we will no longer neglect the backward reaction, but will rather consider the dynamic equilibrium



I assume you know from past studies that a standard model is to assume the backward reaction is “first order” in each of the products, meaning the concentration of ammonium hydroxide increases due to the backward reaction with a rate

$$\frac{d[\text{NH}_4\text{OH}]}{dt} = k_r[\text{H}_2\text{O}][\text{NH}_3].$$

Such a model comes from the assumption that reaction is elementary: that the backward reaction requires H_2O to collide with NH_3 , and that the probability of such a collision would increase linearly in the concentrations of each species. When the reaction occurs in aqueous solution, it is routine to define the effective first order rate constant $k'_r = k_r[\text{H}_2\text{O}]$ since $[\text{H}_2\text{O}]$, the concentration of water in aqueous solution, is effectively constant. Then, we might view the reaction as



(i) You're helping a freshman friend with his general chemistry homework and he keeps referring to k_f , k_r , and k'_r as “rates.” What is wrong with calling all of these parameters rates as opposed to rate constants?

(ii) Your freshman friend tells you about the concept of an equilibrium constant. He says that people like to look at

$$K_{\text{eq}} = \frac{[\text{NH}_3]_{\text{eq}}}{[\text{NH}_4\text{OH}]_{\text{eq}}},$$

where $[\text{NH}_3]_{\text{eq}}$ and $[\text{NH}_4\text{OH}]_{\text{eq}}$ are the long-time equilibrium concentrations. Use the principle of detailed balance at equilibrium (the equality of the rate of NH_4OH production and degradation) to show that K_{eq} can be written in terms of k_f and k'_r .

(iii) Thinking back to Problem 1, you realize that instead of viewing

$$K_{\text{eq}} = \frac{[\text{NH}_3]_{\text{eq}}}{[\text{NH}_4\text{OH}]_{\text{eq}}}$$

in terms of concentrations, you could consider

$$K_{\text{eq}} = \frac{p_{\text{NH}_3}}{p_{\text{NH}_4\text{OH}}},$$

where p_{NH_3} and $p_{\text{NH}_4\text{OH}}$ are the equilibrium probabilities that a single molecule switching between NH_3 and NH_4OH states will occupy each option. This now looks like a partitioning between two possibilities, so you realize K_{eq} must be a ratio of an NH_3 partition function and an NH_4OH partition function. You guess that

$$K_{\text{eq}} = \frac{p_{\text{NH}_3}}{p_{\text{NH}_4\text{OH}}} = \frac{Q_{\text{NH}_3}}{Q_{\text{NH}_4\text{OH}}} = \frac{e^{-\beta A_{\text{NH}_3}}}{e^{-\beta A_{\text{NH}_4\text{OH}}}},$$

implying

$$\Delta A = A_{\text{NH}_3} - A_{\text{NH}_4\text{OH}} = -k_B T \ln \frac{p_{\text{NH}_3}}{p_{\text{NH}_4\text{OH}}} = -k_B T \ln K_{\text{eq}}.$$

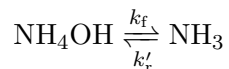
The Q 's are the canonical partition functions and ΔA is the difference in Helmholtz free energy between NH_3 and NH_4OH . You're feeling really pumped about these cool connections you're making

thanks to your new found love of statistical mechanics, but then your freshman friend bursts your bubble. He points you to an equation in his book that reads:

$$\Delta G = -k_B T \ln K_{\text{eq}}.$$

Why does the book have the Gibbs free energy difference ΔG on the left-hand side instead of the Helmholtz free energy difference ΔA ?

(iv) Still working with the effective first-order backward reaction



write down the coupled differential equations for the changes in ammonium hydroxide and ammonia concentrations:

$$\begin{aligned} \frac{d[\text{NH}_4\text{OH}]}{dt} &= \dots \\ \frac{d[\text{NH}_3]}{dt} &= \dots \end{aligned}$$

(v) The solution to the differential equations should take the form

$$[\text{NH}_4\text{OH}](t) - [\text{NH}_4\text{OH}]_{\text{eq}} = ([\text{NH}_4\text{OH}](0) - [\text{NH}_4\text{OH}]_{\text{eq}}) e^{-t/\tau},$$

where $[\text{NH}_4\text{OH}](0)$ is the initial ammonium hydroxide concentration. In terms of k_f and k'_r , what is the time constant τ ?