1. **A chemical decomposition.**

   Consider the decomposition of ammonium hydroxide into ammonia and water:

   $$NH_4OH \rightarrow NH_3 + H_2O.$$

   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 $[NH_4OH]$, $[NH_3]$, and $[H_2O]$ 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.]

   > To still persist after n intervals, the molecule must have survived all of the previous intervals. The probability of survival for each interval is $1 - \alpha$, so the chance of n repeated (independent) survivals is
   >
   > $$p(n\Delta t) = (1 - \alpha)^n.$$

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

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

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

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

   > In the small Δt limit we have
   >
   > $$P(t) = \lim_{\Delta t \to 0} (1 - k_f\Delta t)^{t/\Delta t}$$
   >
   > $$= \left(\lim_{\Delta t \to 0} (1 - k_f\Delta t)^{1/\Delta t}\right)^t$$
   >
   > $$= \left(e^{-k_f}\right)^t$$
   >
   > $$= e^{-k_f t}.$$

(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).

> Differentiating both sides of your answer to (ii) yields:
>
> $$\frac{dp(t)}{dt} = -k_{\mathrm{f}}e^{-k_{\mathrm{f}}t} = -k_{\mathrm{f}}p(t).$$
>
> This looks like the normal first order differential equation we would write down but for the probability of a single ammonium hydroxide molecule staying intact rather than for the concentration of ammonium hydroxide (as we'll see in the next part).

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

$$\frac{d[\mathrm{NH_4OH}]}{dt} = \ldots$$

> The key idea here is that each of the N molecules behaves completely independently of the others. Hence $[\mathrm{NH_4OH}](t) = Np(t)/V$. Taking a time derivative of both sides leads to the rate law
>
> $$\begin{aligned}\frac{d[\mathrm{NH_4OH}]}{dt} &= \frac{N}{V}\frac{dp(t)}{dt} \\ &= -\frac{N}{V}k_{\mathrm{f}}p(t) \\ &= -k_{\mathrm{f}}[\mathrm{NH_4OH}].\end{aligned}$$
>
> This is the standard first-order rate law you are accustomed to writing down, but I've asked you to derive it step by step from simple microscopic assumptions. If you jumped to the result without clear explanations I may have not granted full credit.

(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.)

> We have assumed that all of the ammonium hydroxide molecules are independent. In other words, we have assumed that α is a property that only depends on the single ammonium hydroxide that is going to decompose, not on how many such molecules there are. If, however, the decomposition mechanism involved collisions with other molecules, one should expect the decay probability α to be concentration-dependent. Due to these interactions, concentrations could decay with a different rate law.

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

$$\mathrm{NH_4OH} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{NH_3} + \mathrm{H_2O}.$$
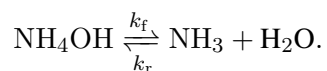
I assume you know from past studies that a standard model is to assume the backward reaction is "first order" in each of the products, meaning the concentration of ammonium hydroxide increases due to the backward reaction with a rate

$$\frac{d[NH_4OH]}{dt} = k_r[H_2O][NH_3].$$

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 $k'_r = k_r[H_2O]$ since $[H_2O]$, the concentration of water in aqueous solution, is effectively constant. Then, we might view the reaction as

$$NH_4OH \underset{k'_r}{\overset{k_f}{\rightleftharpoons}} NH_3.$$
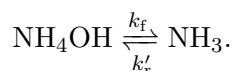
(i) You're helping a freshman friend with his general chemistry homework and he keeps referring to k_f, k_r, and k'_r as "rates." What is wrong with calling all of these parameters rates as opposed to rate constants?

> You could have said several things, but the key thing I wanted you to notice is that they don't even have the same units. While k_f and k'_r do have units of a rate (inverse time), k_r includes a factor with units of inverse concentration. It is the product of the k's with the appropriate concentrations that are actually the rates.

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

$$K_{eq} = \frac{[NH_3]_{eq}}{[NH_4OH]_{eq}},$$

where $[NH_3]_{eq}$ and $[NH_4OH]_{eq}$ 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.

> Detailed balance requires $k_f[NH_4OH]_{eq} = k'_r[NH_3]_{eq}$, so
>
> $$K_{eq} = \frac{[NH_3]_{eq}}{[NH_4OH]_{eq}} = \frac{k_f}{k'_r}.$$

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

$$K_{eq} = \frac{[NH_3]_{eq}}{[NH_4OH]_{eq}}$$

in terms of concentrations, you could consider

$$K_{eq} = \frac{p_{NH_3}}{p_{NH_4OH}},$$

where p_{NH_3} and $p_{\text{NH}_4\text{OH}}$ are the equilibrium probabilities that a single molecule switching between O_2 and H_2O_2 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 O_2 partition function and an H_2O_2 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

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

The Q's are the canonical partition functions and ΔA is the difference in Helmholtz free energy between O_2 and H_2O_2. 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:

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

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

> Which free energy appears depends on the reaction conditions. If the reaction takes place in a fixed volume at constant temperature then the Helmholtz free energy would be appropriate. If however, like most benchtop chemistry, the reaction is carried out with a fixed temperature and fixed pressure, then you should be using a ratio of partition functions that allow for fluctuating volumes, and this change would yield the Gibbs free energy in place of the Helmholtz free energy.

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

$$\text{NH}_4\text{OH} \underset{k_{\text{r}}'}{\overset{k_{\text{f}}}{\rightleftharpoons}} \text{NH}_3$$
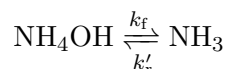
write down the coupled differential equations for the changes in ammonium hydroxide and ammonia concentrations:

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

$$\frac{d[\text{NH}_3]}{dt} = \ldots$$

> $$\frac{d[\text{NH}_4\text{OH}]}{dt} = -k_{\text{f}}[\text{NH}_4\text{OH}] + k_{\text{f}}'[\text{NH}_3]$$
> $$\frac{d[\text{NH}_3]}{dt} = -k_{\text{r}}'[\text{NH}_3] + k_{\text{f}}[\text{NH}_4\text{OH}]$$

(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?

We solved an identical problem in class. If you just remembered that $\tau = (k_f + k'_r)^{-1}$ that was fine. I assumed most people would not remember this and would have to rederive the result. You could look in the notes to see how we did this in class. An alternative method that you might have figured out based on the homework, is to inspect the eigenvalues by solving

$$0 = \begin{vmatrix} -k_f - \lambda & k'_r \\ k_f & -k'_r - \lambda \end{vmatrix} = \lambda^2 + (k_f + k'_r)\lambda + k_f k'_r - k_f k'_r.$$

This eigenvalue equation is solved when $\lambda = 0$ (an eigenvalue associated with equilibrium) and when $\lambda = -(k_f + k'_r)$. This second eigenvalue implies an exponential decay of the form

$$e^{-(k_f + k'_r)t},$$

which is enough to answer the question.

3. **Do you smell that?** I'm worried people are going to fall asleep in lecture, so I decide to open up a bottle of perfume at the front of the room the moment I see someone start to nod off. Let's try to figure out how long it will take before they smell it.

(i) Let us first assume that the random walk models we've worked so laboriously to understand can help us explain the situation! In other words, we assume that each perfume molecules can be modeled as moving in some direction until it collides with an air molecule, at which point the perfume randomly gets kicked in a new directly. We have seen that the spread of the random walkers (in this case perfume molecules) goes like $\langle \delta \boldsymbol{R}^2 \rangle_T = 2dDT$, where d is the dimensionality and D is the perfume's diffusion constant. Since we live in a three dimensional world, $\boldsymbol{R}^2 = X^2 + Y^2 + Z^2$ and $d = 3$. If perfume has a diffusion constant in air of 10^{-6} m^{2}s^{-1}, estimate the time for the perfume to reach the dozing student 5 meters away.

Your first hunch may be that the typical distance traveled by a particle is $\langle \boldsymbol{R} \rangle$, but if the particle is moving due to pure diffusion (not diffusion plus drift), notice that $\langle \boldsymbol{R} \rangle = 0$ by symmetry. Even when the mean isn't moving, it's clearly not the case that most particles aren't going to move. Thus we will measure the "typical distance" that the particles move by the root mean squared: $R_{\text{rms}} \equiv \sqrt{\langle R^2 \rangle_T} = \sqrt{\langle \delta \boldsymbol{R}^2 \rangle_T}$ (assuming that we have pure diffusion with $\langle \boldsymbol{R} \rangle = 0$ on this last equality). Solving for $R_{\text{rms}} = \sqrt{6DT} = 5$ meters gives $T \approx 4 \times 10^6$ seconds!

(ii) Is your answer to (i) reasonable? What else could be going on?

Our answer to (i) is about an eighth of a year. There is no way that is consistent with our experience (but think of how much more pleasant that could make walking through a department store). It seems our assumption that the motion is due to pure diffusion is probably not valid. Rather, there are "convective currents" due to slight temperature variations around a room.

(iii) While we're crunching numbers, let's think about the *self-diffusion* of water, that is to say one molecule diffuses in a background of other water molecules (as opposed to the perfume in a background of air). The self-diffusion constant for a water molecule in liquid water is about 10^{-5}cm^2/sec. Assuming the liquid is at equilibrium and not stirred, what are the typical times for a water molecule to move one molecular diameter (about 0.3 nm)? What about across the surface of a protein (about 1 nm)? Finally, a macroscopic distance (about 1 cm)?

This problem just required you to plug some numbers in to get a sense of timescales that are important to chemistry. To move one molecular diameter requires about $(0.3 \text{ nm})^2/(6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) = 15 \text{ ps}$. Diffusing across the surface of a protein requires about $(1 \text{ nm})^2/(6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \approx 167 \text{ ps}$. Finally, to diffuse 1 cm requires about $(1 \text{ cm})^2/(6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \approx 4.6 \text{ hours}$.