

Experiment 1: Probability and Equilibrium

Objectives: To gain a clear idea of how equilibrium and probability are related; to review Le Chatelier's Principle; to see how the work of scientists often requires small efforts by a large number of individuals.

Reference: IMT, Chapter 1.

Logistics: Work in teams of two or three, (8 or 10 teams per lab section) taking turns to shuffle, record, and check data. You will also be responsible for recording the data from your section as a whole.

Prelab Preparation: See the general requirements listed in the introductory pages. Read over the experiment carefully -- more than once -- before coming to lab. Answer the following questions:

1. Determine the expected equilibrium constants for equations (1) and (2).
2. Predict what will happen in each part: A, B, and C.
3. Be sure you understand the model we are using. Why do we not include the nitrogen and oxygen atoms in the calculation?

Modeling Equilibrium

One of the most successful areas of chemistry, and one that is growing rapidly, is the field of *modeling*. In modeling, computers (usually) are used to simulate actual chemical reactions. For example, biochemists studying how hemoglobin interacts with O₂ in the blood can construct a three-dimensional model of hemoglobin at a small computer workstation and study how the atoms fit together to transport oxygen. Sometimes simulation is the only way to test out a theory or study a complicated system. For example, it was largely as a result of simulations carried out by atmospheric chemists that the plight of ozone (O₃) in our atmosphere has become a matter of public policy. In this experiment *you* will act as the computer to simulate a chemical equilibrium.

Last term you learned that all equilibria have an associated equilibrium constant, and that this constant was some number. For example, for the dissociation of water into H⁺ and OH⁻ at 25 °C, K_{eq} = 1.0 x 10⁻¹⁴. This semester you will gain insight into *why* equilibrium constants are the numbers that they are. Why so large? Why so small? There are very good reasons that have to do with probability and energy. In this experiment you will study the probabilistic aspects of equilibrium, focusing on two specific *isotope exchange* reactions:



Here “H” is ¹H and “D” is ²H, deuterium. Based on these reactions, The reaction quotients based on these equations can be written:

$$Q_1 = \frac{[\text{HDO}]^2}{[\text{H}_2\text{O}][\text{D}_2\text{O}]} \quad Q_2 = \frac{[\text{NH}_2\text{D}][\text{NHD}_2]}{[\text{NH}_3][\text{ND}_3]}$$

Remember, *Q* can be measured at any time during a reaction. *Q* = 0 when at least one of the

substances on the right side is missing; $Q = \infty$ when a substance on the left is missing. No matter what Q is when you start a reaction, it will continue to change for a while and then stop changing. The final value for Q when everything stops changing is what we call the *equilibrium constant*, K . This relationship between Q and K is often summed up as follows:

$$\begin{aligned} Q &= K \text{ at equilibrium} \\ Q < K &\text{ means too much reactant} \\ Q > K &\text{ means too much product} \end{aligned}$$

The main point of Chapter 1 of *Introduction to Molecular Thermodynamics* is that Q really should fluctuate, because equilibrium is based on probability, and what we call the equilibrium state is simply the “most probable” state. Equilibrium is like the constant shuffling of a deck of cards. Furthermore, the amount of fluctuation is a function of how many particles we are dealing with. Now is your chance to investigate this yourself. What you will be doing will be a true *experiment*. You will use playing cards to model the water and ammonia isotope exchange reactions as described more fully below.

Le Chatelier's Principle

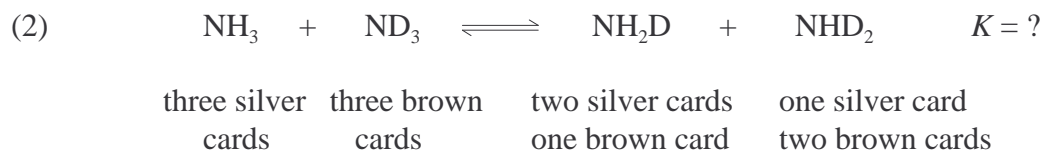
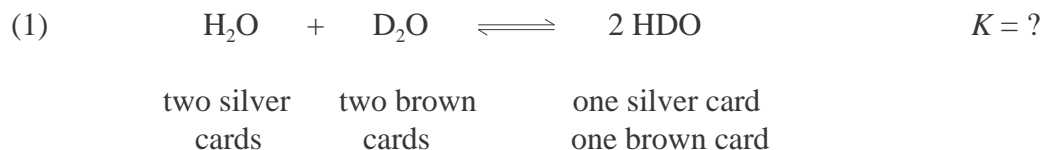
In addition, remember Le Chatelier's Principle? If a reactant is added to an equilibrium mixture, Q will suddenly be less than K , and the reaction will shift to the right to re-establish $Q = K$. We will test Le Chatelier's Principle using playing cards to see if it, too, arises from probability.

The Model

We have two kinds of playing cards; some have brown backs, some have silver. Here is the metaphor:

H atoms	silver
D atoms	brown
water molecules	“hands” of two cards with an implied O atom holding them
ammonia molecules	“hands” of three cards with an implied N atom holding them

The equilibrium reactions, then, are as follows:

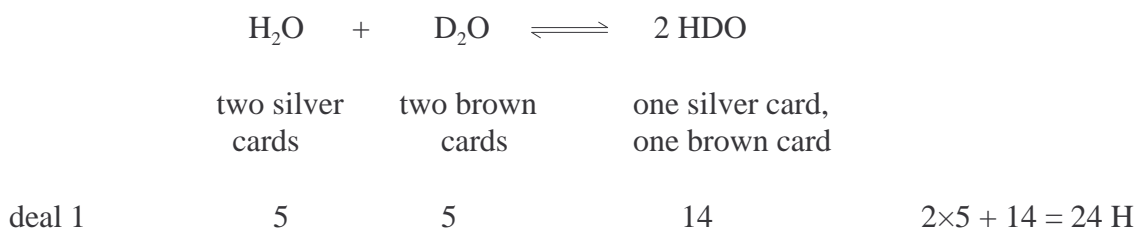


Data Collection

A. Isotope Exchange in Water

Read this entire section before you begin, or you will double your workload.

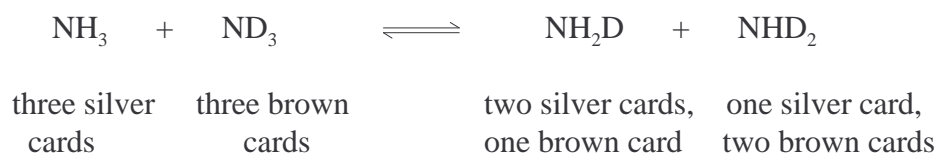
For the first reaction, make up a deck of 24 silver and 24 brown cards. The silver cards represent H atoms; the brown cards represent D atoms. After shuffling well (seven times minimum, please), deal out two-card hands face-down so you can see the colors. Deal into piles, depending upon what turns up: pairs of silver cards in the first pile, pairs of brown cards in the second pile, and mixed brown/silver pairs in a third pile. If you do this neatly, it will be easy to count the hands. When all of the cards are dealt, record the number of H₂O, D₂O, and HDO molecules in your notebook. Be sure to check that the overall number of H atoms recorded is 24. For example:



Don't forget to actually add up the number of H atoms! If the numbers don't add up, just draw a line through the data and repeat that deal. Repeat this process for a total of **eight** times, shuffling at least seven times between deals. Leave room in your notebook for a few more deals, just in case you made an error that you catch later. In addition, leave room for a line which totals all of the deals for each kind of molecule.

B. Isotope Exchange in Ammonia

For the second reaction, repeat the shuffling and dealing, this time dealing out 16 hands of *three* cards each and separating them into four different piles:



Again, record your data. Here checking your numbers is very important, as it is very easy to make a mistake. Be careful to check that the number of H atoms *total* (3 for each NH₃, 2 for each NH₂D, 1 for each NHD₂) is 24. If you find an error, just draw a line through the data and repeat that deal. Repeat this process for a total of **eight** times. Again, leave room in your notebook for correction of errors and also a line which totals all of the deals for each kind of molecule.

C. Le Chatelier's Principle

To investigate whether Q at equilibrium does always equal K_{eq} , we need to “stack” the decks. Link up with another team to share data for this part. One team should collect data for water while the other collects data for ammonia. Make certain you get all of the data for both groups' work in your notebook. Depending upon which reaction you look at, you will repeat either Part A (as C1) or Part B (as C2):

	(C1) water reaction	(C2) ammonia reaction
deck:	24 H atoms, 48 D atoms (24 silver, 48 brown)	54 H atoms, 27 D atoms (54 silver, 27 brown)
initial state:	$12 \text{ H}_2 + 24 \text{ D}_2 + 0 \text{ HDO}$	$18 \text{ NH}_3 + 9 \text{ ND}_3 + 0 \text{ NH}_2\text{D} + 0 \text{ NHD}_2$

Set up your deck as indicated. Note that in both cases, since we start with no product, Q is 0. Then carry out the reaction nine times, repeating the procedure that you used in Part A or Part B, as appropriate. This time, though, shuffle only once between deals and do not lay out your types of molecules in separate piles. This time have someone in your group tally the number of each type of molecule but leave all of the cards in one pile. This allows you to observe the effect of “stacking” the deck. Leave room in your notebook for a “total” line as well as for copying the other team's data; but this time **do not include your first two deals in the totals**.

Data Analysis

There will be three stages in the analysis of your data:

1. First, you need to calculate Q for each deal that you made. There will be much variation, including some (probably) which give $Q = 0$ or $Q = \infty$.
2. Second, you need to calculate Q for the total of all of your deals in each part, A, B, C1, and C2 (remember that in C1 and C2 you should not include the first two deals in your totals). This approximates the shuffling of a much larger deck. Use these values as your team estimates of K for the water and ammonia isotope exchange equilibria.
3. Next, you need to total all of the deals of all of the teams in your section and calculate Q for each part. This final collection of data will be done by computer. Four spreadsheets will be set up, one for each of the parts, A, B, C1, and C2. Your team should enter your “bottom line” information from each part onto the appropriate spreadsheet. The spreadsheet will automatically check that your Hs and Ds add up. If they don't, you must recheck your work: Do the H's in each line of your data really add up? Is there an addition error in calculating the totals? Some repeat dealing may be required to fix your data. Record in your notebook all of the spreadsheet data for your section. Use your section's “bottom line” for your final estimate of K for the water and ammonia isotope exchange equilibria. Again, none of the computer tallies should include the first two deals of C1 or C2.

Don't leave the room until this is done!

Discussion

1. Summarize your team's findings in Parts A and B: What was your team's best estimate for K for the water isotope exchange reaction? For the ammonia reaction? Did you see quite a fluctuation in Q ? How do your values for K compare with the values of K for each reaction based on your section's overall bottom line?
2. Compare your own data with that from your section in terms of fluctuation in Q . Discuss this fluctuation in terms of probability.
3. Based on the data collected in parts C1 and C2 by your team and the team you paired up with, did Q generally increase as the reaction proceeded (from one shuffle to the next), approaching (perhaps) K ? (Remember, even if it did reach K , there would be some fluctuation, right?)
4. Why did we ask you to exclude the first two deals from the total line for parts C1 and C2? What changes in your results would you expect if you had included these two pieces of data?