

Using a Spreadsheet to help the teaching of
Chemical Equilibrium

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1. INTRODUCTION

1.1 THE TOPIC - WHY EQUILIBRIUM?

Chemical equilibrium is a key concept in all advanced chemistry courses. Unfortunately it is also one that many students find difficult - possibly for three main reasons:

1. Everyday, static notions of equilibrium and balance appear to be so deeply entrenched in students' minds that they find great difficulty appreciating the dynamic aspects of chemical equilibrium
2. Chemists explain and use the equilibrium concept in a number of very different ways and it can be difficult for students to see the connection between these - or even to realise that they are the same idea. These worksheets are designed to tackle this problem by providing an environment within which the various approaches can be integrated.
3. Although real understanding of science concepts is essentially qualitative it is expressed in many mathematical relations. Most students of equilibrium therefore spend a great deal of time and effort doing calculations. These demands of these calculations can be of two kinds:

- some of the mathematical models involved are complex
- there is a need for repetitive analysis of large amounts of data

and both of these can serve to focus students' attention on mechanical mathematics at the expense of their understanding of the underlying scientific principles. This a serious hindrance to students' learning.. The need therefore is for a tool or tools that can be used by the pupil to model simple systems, allowing them to express their understanding of the science involved and by the teachers to construct more complex models for the students to explore.

1.2 THE TOOL - WHY A SPREADSHEET?

Spreadsheets have a number of attributes which make them suitable for use as a computational tool in the school laboratory, the most important of which are their flexibility and their (increasingly) well integrated graphing facilities making them capable of being used as a powerful, flexible and widely available microworld within which students can interact with models to both express their own understanding of a situation and explore the meanings of others.

Much of chemistry, especially physical chemistry, is concerned with building, and exploring mathematical models of aspects of the world. Since their invention computers have been used to aid this process, most often by means of specially written simulations of processes and events. Virtually all of these simulations are computationally based (as opposed to rule-based simulations used in Expert Systems). However in most cases the mathematical models on which the simulation is based are not only fixed, and thus not capable of being changed by the student, but are not even available for inspection. Students are thus reduced to manipulating an inputs to see their effects. of course there is a role for such models but we believe that much is to be gained from allowing students to interact with an environment in which they can produce and run their own models - or at the very least where the models they are exploring are open, available to inspection and modification. It is important therefore to draw a distinction between two kinds of tool:

- Closed - which are invariably simulations and where the student only has control of (some of) the inputs. Using models in this way students can explore the ideas of others. Therefore this method of use is often called 'exploratory'.
- Open - which may be pre-written simulations where the student can inspect and modify the model but may also be 'content free shells' within which students can write their own models. Using models in this way students can express their own ideas. Therefore this method of use often called 'expressive'.

The examples given here hope to show that spreadsheets can be used (by teachers and/or students) to build models in both these modes of use.

In thinking about the range of kinds of model that students can use to aid their developing understanding of the equilibrium concept, two other distinctions are important. These are the static/dynamic and deterministic/probabilistic dimensions.

- Static/dynamic. A static model is one that can only be run once - to give a single result on a given data set. An example of this is when students are asked to construct their own models of the equilibrium law expression given experimental values for equilibrium concentrations. By contrast a dynamic model can show how a situation changes over time, for example how concentrations change as a reaction proceeds or as increasing quantities of one reagent are added. Spreadsheets can be used to build dynamic models in two ways. One is to have a series of static models each of which takes as its initial values the results of the previous calculation. The change of such values over time can then be illustrated by means of a graph. An example of this is following the progress towards equilibrium of two competing reactions. A second way is to use the ability of spreadsheets to perform iterative calculations and display successive values of the same variable in one cell. An innovative use is seen in the Monte-Carlo model in which, once the reaction starts, a diagrammatic representation of the changing amounts of each species is continuously displayed.
- Deterministic/probabilistic. Virtually all models and simulations used in teaching chemistry are deterministic, that is a set input will always produce the same output. However, at heart chemical change is determined by **probability**. In reality it is only possible to give deterministic results because the numbers of species involved are so huge that probability become certainty. We feel that it is important that students are given some understanding of this important truth about the nature of chemical change and for this reason we have included one probabilistic examples - the Monte-Carlo model of equilibrium.

Often different tools have to be used to implement each of the different kinds of model. The examples that follow are designed to show that spreadsheets are flexible enough tools to be used to build models falling anywhere along these three dimensions. They therefore offer the possibility of providing an integrated environment within which students can explore the different approaches and ideas associated with the equilibrium concept.

1.3 THE FUTURE

The worksheets used here are a first attempt and one of the main objectives of the current work is to see which (if any) are worth further development. In addition, to be fully effective,

they should be linked by a suitable organising environment which would allow students to move easily between them and provide appropriate context-sensitive help and advice.

2. THE EXAMPLES - EQUILIBRIUM LAW DETERMINATION AND USE

This section describes the worksheets which have been developed to meet the aims outlined above. It includes a description of each worksheet, the concept or idea it is designed to help teach and some ideas for classroom use. However it is essential to remember that the purpose of the trials is to develop and evaluate ideas and approaches for classroom implementation and that the suggestions included here are just that - suggestions to be modified or abandoned depending on the circumstances.

2.1 EQUILIBRIUM LAW DETERMINATION

Students often have trouble understanding why the equilibrium law has the form that it does and teachers often try to overcome this by encouraging them 'discover' it for themselves by experimenting with sets of previously obtained equilibrium concentrations. One simple example is to give data for the hydrogen/iodine/hydrogen iodide system and to ask the students to find a pattern in the relationship between the numbers. The problem here is that a lot of repetitive calculations are involved, the boring mechanics of which limits the number of models which can be explored and gets in the way of the ideas being developed. It can also give the students the idea that physical chemistry is about 'doing sums' rather than exploring ideas using mathematical models. However this is an ideal example for the students to do their own modelling as both the mathematics and the models are simple.

Experience suggests that this is a good example to use with students who are new to spreadsheets as it allows them to get used to entering data and using the 'Copy' or 'Fill Down' commands.

The equation for the reaction is:



And typical models produced by student, are:

$$\text{K1:}([\text{H}_2]+[\text{I}_2])/[\text{HI}] \quad \text{K2:}[\text{H}_2] * [\text{I}_2]/[\text{HI}] \quad \text{K3:} [\text{H}_2]*[\text{I}_2]/([\text{HI}]^{\wedge}2)$$

These represent the most common misconceptions but it is important that students write their own models either working in groups of two or three or, with a small class, at one computer following a whole-class discussion.

Initially the worksheet just contains the columns of data and blank columns for the student models. To use the worksheet, the students enter formulae representing **their** models in the top cell of each column and then copy them down to the rest. Simply looking at the results allows them to see which model produces a constant value for the equilibrium constant.

Two points that probably need to be discussed with the class:

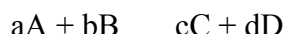
1. **No** model produces exactly the same value for the equilibrium constant in all cases. This is because the numbers are real experimental data and it is interesting to discuss how constant the value for K has to be before we can call it a constant.

2. **Two** expressions will give a constant value for K - $[H_2][I_2]/([HI]^2)$ and $([HI]^2/[H_2][I_2])$. This can be used to introduce the convention of writing the concentrations of the products on the numerator and for demonstrating that it is a convention.

Figure 1: A typical example of a worksheet produced for the H₂/I₂/HI system

Hydrogen	Iodine	Hydrogen iodide	K1	K2	K3
4.56	0.74	13.54	4.61	0.125	0.18
3.56	1.25	15.59	3.64	0.143	0.18
2.25	2.34	16.85	2.39	0.156	0.19
0.48	0.48	3.53	0.62	0.033	0.18
0.50	0.50	3.66	0.64	0.034	0.19
1.14	1.14	8.41	1.27	0.077	0.18

Once the students have produced a constant value for K, they can be encouraged to try to generalise their ideas. The worksheet contained data for the Ethanol/ Ethanoic acid/ Ethyl Ethanoate/Water system - a four component system - and students could be asked to produce a K value for this system and compare the equations that produce a constant value in the two cases. The idea is to lead students to think what the general form of this expression could be - i.e. for equations of the type:



Points to be evaluated here include:

- how easy the students found it to try out different expressions
- the variety of ideas and models tested
- whether the students understood and remembered the Equilibrium Law better than using traditional methods.

2.2 EQUILIBRIUM LAW USE

2.2.1 STEPWISE CALCULATION OF EQUILIBRIUM CONCENTRATIONS

Having seen how the equilibrium law is determined students could be given an exercise to use it. The worksheet shown below is derived from one given in an article by Jon Ogborn¹ and can be used to perform 'brute force' calculations of the composition of equilibrium mixtures. When the spreadsheet is instructed to re-calculate it 'reacts' the amount indicated in the box; shows the amount of reactants and products after the reaction and calculates the 'equilibrium constant' at the concentrations shown. The

amounts of reactants and products can be altered by telling the system to react different amounts until the calculated equilibrium constant matches the book value. The amounts of reactants and products shown are then those which would be present at equilibrium. The amounts of reactants can be increased by telling the system to react a negative amount, i.e. 'go backwards'.

Essentially the worksheet multiplies the amount it is told to react by the stoichiometry of each component and subtracts the result from (for reactants) or adds it to (for products), the existing amount of that component. It then uses these amounts, together with the known stoichiometry to calculate an 'equilibrium constant'. Note that this simple model takes no account of changes in volume, although in the particular case shown this does not matter as the volume terms cancel out in the equilibrium constant expression.

Figure 2: Ethanol/Ethanoic Acid/Ethyl Ethanoate/Water system

React	<input type="text" value="0.001"/> moles			
Name	Ethanol	Ethanoic Acid	Ethyl Ethanoate	Water
Stoichiometry	1	1	1	1
Initial []	1	1	0	0
Total change	0.671	0.671	0.671	0.671
Current	0.329	0.329	0.671	0.671
	Book Value		Calculated value	
	Kc	4.00E+00	K	4.16E+00
	lnKc	1.39E+00	lnK	1.43E+00

The key cells are those which multiply the contents of the 'amount to react' box by the relevant stoichiometry and subtract (for reactants) or add (for products) the result to the existing contents of the box. (See Table 1 in the Appendix for the formulae used.)

This idea can be easily extended to other examples, showing the effect of various stoichiometries and initial concentrations on equilibrium concentrations. One advantage of such calculations is that they can help rectify the commonly held belief reported by Gorodetsky and Gussarsky² and Hackling and Garnett³ amongst others that at equilibrium the concentration of every component of the mixture is either the same or in proportion to the stoichiometry of the reaction.

Figure 3: Solubility of Lead Chloride in pure water

Volume (mL) Dissolve moles

Name	Lead ions	Chloride ions
Stoichiometry	1	2
Initial []	0	1
Total change	7E-05	0.00014
Current	7E-05	1.00014
	Book Value	Calculated value
	Ksp 2.00E-05	K 7.00E-05
	lnKsp 1.08E+01	lnK 9.57E+00

One way in which the model may be adapted is shown in Figures 3 and 4 in which the equilibrium concentrations of a solution of a sparingly soluble salt are in the process of being calculated using the K_{sp} value. This is particularly interesting as it allows an easy simulation of the common ion effect. The concentrations of lead and chloride ions present when lead chloride is dissolved in pure water (being calculated in Fig 3) can be compared with those obtained when it is dissolved in a solution initially 1 mol/dm^{-3} in chloride ions (shown in Fig 4) simply by altering the values in the 'initial concentration' box.

The structure of the worksheet is exactly the same as in the previous example the only changes are to the titles of some of the cells.

Figure 4: Solubility of Lead Chloride in a solution 1M in Chloride ions

Volume (mL) Dissolve moles

Name	Lead ions	Chloride ions
Stoichiometry	1	2
Initial []	0	1
Total change	2E-05	4E-05
Current	2E-05	1.00004
	Book Value	Calculated value
	Ksp 2.00E-05	K 2.00E-05
	lnKsp 1.08E+01	lnK 1.08E+01

Substituting (using equations 3-5), and rearranging gives

$$[A^-] = (K_a \cdot C_a \cdot V_a) / (V_f (K_a + [H^+])) \quad (7)$$

Similarly $[B^+] = (K_b \cdot C_b \cdot V_b) / (V_f (K_b + [OH^-])) \quad (8)$

Using equations 7 and 8 to substitute for $[A^-]$ and $[B^+]$ in equation 6, using equation 1 to eliminate $[OH^-]$ and simplifying gives

$$f[H^+] = V_f + C_b V_b / ((K_w / K_b) + [H^+]) - V_f K_w / [H^+]^2 - K_a C_a V_a / ([H^+] (K_a + [H^+])) = 0$$

The derivative of $f[H^+]$, $f'[H^+]$ is

$$C_b V_b / (K_w / K_b + [H^+])^2 + 2 V_f K_w / [H^+]^3 + K_a C_a V_a (K_a + 2[H^+]) / ([H^+] (K_a + [H^+])^2)$$

2.2.2.3 The Worksheet

Figure 5 shows the worksheet constructed to implement this approach for the reaction between ethanoic acid and aqueous ammonia.

Figure 5: Modelling an acid-base titration

Initial Data	[Acid]	K _a	Volume	[H ⁺] estimate
	1.00	1.70E-05	10.00	1.00
	[Base]	K _b	K _w	Max Error
	1.00	1.80E-05	1.00E-14	1.00E-15
Titration	Add	<input type="text" value="0.01"/>	mL of base	
Result	Vol. base added	Total Vol.	[H ⁺]	[OH ⁻]
	10.01	20.01	8.90E-08	1.12E-07
<input type="text" value="pH = 7.05"/>				

A function macro (an annotated listing of which is shown in Table 2 in the appendix), which is called from the '[H⁺]' box performs the iterative calculations and returns the result when the difference between successive iteration is less than the value set for the maximum error. The contents of the other boxes are either set by the user or are derived from the calculated value of [H⁺]. The macro showed a distressing tendency to converge on a very large positive root when the pH rose above 7. This was stopped by checking whether the calculated concentration of [H⁺] was greater than the initial concentration of acid and if it was, then starting the iteration again with $G_1 = 10^{-14}$. This ensured that a chemically meaningful result was obtained.

2.2.2.4 Classroom use

It is **not** suggested that students are asked to programme the macro that runs this worksheet! Instead this example is meant to be used in an exploratory mode where students enter the data for a number of reactions with acids and bases of varying strengths and see how the pH varies during each 'titration'.

Perhaps most benefit can be gained by using the model together with a experimental investigation of the same system, possibly trying some of the activities listed below:

1. After each aliquot is added to the reaction mixture students can 'react' a similar amount on the worksheet and compare the experimental and theoretical results.
2. Graphs of both theoretical and experimental results can be plotted to show how the pH varies when acids and bases of different strengths are reacted.
3. Once the students have seen that the theoretical results are in agreement with those obtained by experimentation they can use the worksheet alone to
 - a explore a wider range of reactions than are available in the laboratory
 - b look at pH changes around the equivalence point in more detail than is experimentally possible. Using the worksheet the aliquot size can be made as small as desired.
4. The shape of the pH curve suggests that something very dramatic happens at the equivalence point. it is instructive for students to use the data displayed in the worksheet to plot the way the **concentrations** of $[H^+]$ and $[OH^-]$ vary as the titration proceeds. This is something not usually done from experimental data (possible because of the calculations involved) and most students find the graphs obtained surprising. Their surprise can lead to very interesting and productive discussions concerning the logarithmic nature of pH. It is often believed that a big change in $[H^+]$ indicates a big change in absolute concentration. inspection of the graphs obtained in this exercise shows this not to be true. The whole of the big change in pH around the equivalence point is produced by a concentration change of less than about 10^{-4} mol/L. This allows the point to be made that big differences in pH measures big changes in the ratio of the $[H^+]$ in the two solutions.

Two final points:

1. The worksheet is presently limited to monobasic acids and bases.
2. It is possible to 'unreact' some base by putting a negative value in the 'Add' box. This feature is very useful in exploring around the equivalence point since if a student goes too far, he/she can just unreact the amount they have just added and try again with a smaller aliquot.

3. THE EXAMPLES - EQUILIBRIUM AS COMPETING REACTIONS

A second way of explaining equilibrium is to say that it exists because two or more competing reactions are taking place. The simplest example of this is where there are two first order reactions and this is what is developed below. However once this is built, students can begin to incorporate additional variables - allowing for variable rate constants, temperature dependence and second and higher order reactions. Time and the students ability are the only constraints!

Dynamic models such as this are particularly effective when the graphics function is used as the student can then see a picture of the way in which the rate changes as equilibrium is approached and/or some variables are altered. Good variables to play with are starting concentrations and rate constants. This is a much more effective and dynamic way of seeing change than looking at columns of figures.

Figure 6: Simple example of equilibrium as competing reactions.

[A]	kF	d[A]	[B]	kB
100.00	0.20		0.00	0.20
100.00	0.20	20.00	0.00	0.20
80.00	0.20	16.00	20.00	0.20
68.00	0.20	13.60	32.00	0.20
60.80	0.20	12.16	39.20	0.20
56.48	0.20	11.30	43.52	0.20
53.89	0.20	10.78	46.11	0.20
52.33	0.20	10.47	47.67	0.20
51.40	0.20	10.28	48.60	0.20
50.84	0.20	10.17	49.16	0.20
50.50	0.20	10.10	49.50	0.20
50.30	0.20	10.06	49.70	0.20
50.18	0.20	10.04	49.82	0.20
50.11	0.20	10.02	49.89	0.20
50.07	0.20	10.01	49.93	0.20
50.04	0.20	10.01	49.96	0.20
50.02	0.20	10.00	49.98	0.20
50.01	0.20	10.00	49.99	0.20
50.01	0.20	10.00	49.99	0.20
50.01	0.20	10.00	49.99	0.20
50.00	0.20	10.00	50.00	0.20

This is an iterative model in which the initial concentrations of A and B are set as are the rate constants. (the values in the solid boxes.) Each line represents one unit of time in which some A reacts reducing its concentration by an amount d[A] (found by multiplying [A] by the rate constant kF) and increasing the concentration of B by a similar amount. At the same time B is reacting, reducing its concentration and increasing that of A by d[B]. The new concentrations of A and B are thus:

$$[A]_2 = [A]_1 - d[A] + d[B]$$

$$[B]_2 = [B]_1 - d[B] + d[A]$$

This process is repeated on each line of the worksheet, and as expected (given that the two rate constants are the same) the concentrations of the two species converge.

Many features of this model are worth close inspection, such as the relationship between the rates of the forward and reverse reactions and the equilibrium concentrations and hence the equilibrium constant. It is particularly interesting to contrast this 'rate based' equilibrium model with the stochastic model described in section 5 and to allow students to see how these apparently totally distinct kinds of model are just different ways of looking at the same phenomenon.

Figure 7 shows the concentration/time graph obtained from the data given in Figure 6 - i.e. where the rate of the forward and reverse reactions are the same. If one of the rate constants is changed (say k_B is halved) this is immediately reflected in the graph (Figure 8) - in this case it is easy to see that if the rate constant for the reverse reaction is half that for the forward reaction then B has an equilibrium concentration twice that of A.

Figure 7: Concentration/time graph for a reversible reaction with equal rate constants

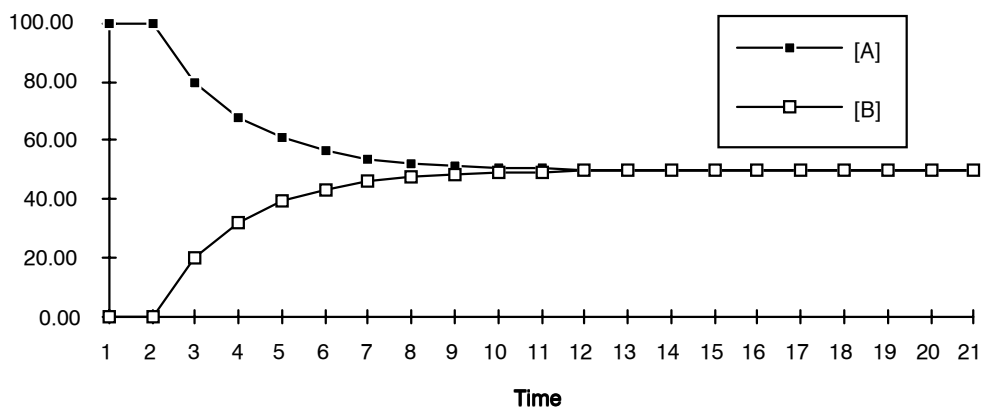
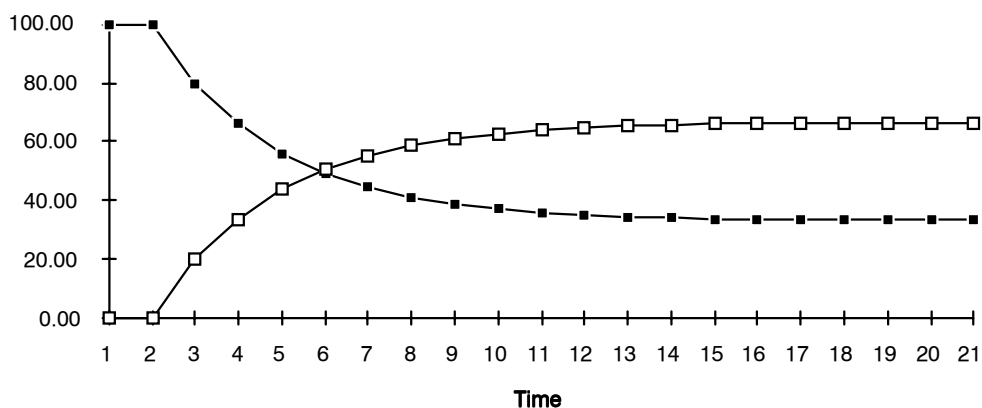


Figure 8: Concentration/time graph for a reversible reaction with unequal rate constants



(A listing of the formulae used in the worksheet is given in Table 3 of the Appendix.)

4. THE EXAMPLES - EQUILIBRIUM AS MAXIMUM TOTAL ENTROPY

4.1 INTRODUCTION

One vital aspect of chemical equilibrium is that the position of equilibrium is the extent of reaction where the total entropy change (of system plus surroundings) is at a maximum. The calculations involved in determining how the total entropy changes as a reaction proceeds are formidable and far too time consuming for student to perform. This worksheet automates this process and allows a number of important ideas to be demonstrated.

In addition to showing that equilibrium corresponds to the position of maximum entropy it also illustrates the different ways in which changes in concentration/pressure and temperature affect equilibrium mixtures. The problem is that both of these variables change the equilibrium concentrations and we often speak of both 'changing the position of equilibrium'. However they affect the equilibrium in very different ways - while temperature changes the equilibrium constant, pressure/concentration does not. This worksheet allows these different affects to be seen and explored.

The structure of the worksheet allows it to model virtually any gas or homogeneous liquid phase reaction for which the thermodynamic data is available. In particular it can be used when there is either one or two products. However, for simplicity only one reaction is described in detail - the Haber process reaction.

4.2 PRODUCING THE WORKSHEET

The worksheet shown here uses the standard molar enthalpies and entropies of the reactants and products to calculate the total entropy change at different extents of reaction at the given temperature and pressure. It is a development of an earlier worksheet⁵ which was restricted to the Haber process reaction, the main difference is that in the sheet given here all the main thermodynamic quantities are treated as variables in the calculations so that the sheet can be easily used for different reactions simply by inserting the relevant data in the box at the top. To allow students easily to see what data they need to enter and what is calculated by the former are in bold while the latter are in plain type.

Three points about the thermodynamic values used:

1. A temperature of 400K and a pressure of 10atm were chosen so that a discernible maximum could be easily seen. Under these conditions the equilibrium constant is 40.7 and about .9 of the nitrogen has reacted.
2. The value of the equilibrium constant varies rapidly about this point and is **extremely** dependent on the values of the precise values of the thermodynamic constants chosen. Because one is looking at very small differences between large quantities variations on the third or fourth significant figure of the molar enthalpies and entropies can have very disproportionate effects on the equilibrium constant found.
3. Any discussion of thermodynamic quantities requires the specification of a reference zero. This of course can be chosen arbitrarily so the most natural zero was chosen, that of a mixed but unreacted stoichiometric mixture of hydrogen and nitrogen. In this way the entropy **change** as the reaction proceeds can be easily seen.

(The formulae used to produce the worksheets are listed in Figure 4 in the Appendix)

Figure 9: Entropy changes during the Haber process reaction at 10atm and 400K

Reacting Entities	Reactant 1	Reactant 2	Product 1	Product 2
Name	Nitrogen	Hydrogen	Ammonia	0
Stoichiometry	1	3	2	0
Standard molar entropy	192	131	192.45	0
Standard molar enthalpy	0.00	0.00	-46.11	0.00
Initial Amount (mol)	1	3	0	0
Initial partial pressures	2.5	7.5	0	0
xLN(x)	2.29	15.11	0.00	0.00

Reaction Conditions

Temperature (K)	400
Step size	0.01
Pressure	10.00

Initial Values

Extent of reaction	0.65
'Enthalpy'	-92.22
'Entropy'	-284.04

ξ	Pr1	Pr2	Pp1	Pp2	nt	Ssur	Ssys	Stot	"K"
0.65	1.30	3.89	4.81	0.00	2.70	149.86	708.92	858.77	0.30
0.66	1.27	3.81	4.93	0.00	2.68	152.16	707.02	859.19	0.35
0.67	1.24	3.72	5.04	0.00	2.66	154.47	705.12	859.59	0.40
0.68	1.21	3.64	5.15	0.00	2.64	156.77	703.20	859.98	0.46
0.69	1.18	3.55	5.27	0.00	2.62	159.08	701.27	860.35	0.52
0.70	1.15	3.46	5.38	0.00	2.60	161.39	699.33	860.72	0.61
0.71	1.12	3.37	5.50	0.00	2.58	163.69	697.38	861.07	0.70
0.72	1.09	3.28	5.63	0.00	2.56	166.00	695.42	861.41	0.82
0.73	1.06	3.19	5.75	0.00	2.54	168.30	693.44	861.74	0.96
0.74	1.03	3.10	5.87	0.00	2.52	170.61	691.45	862.06	1.13
0.75	1.00	3.00	6.00	0.00	2.50	172.91	689.44	862.36	1.33
0.76	0.97	2.90	6.13	0.00	2.48	175.22	687.43	862.64	1.59
0.77	0.93	2.80	6.26	0.00	2.46	177.52	685.39	862.92	1.90
0.78	0.90	2.70	6.39	0.00	2.44	179.83	683.34	863.17	2.29
0.79	0.87	2.60	6.53	0.00	2.42	182.13	681.28	863.41	2.78
0.80	0.83	2.50	6.67	0.00	2.40	184.44	679.20	863.64	3.41
0.81	0.80	2.39	6.81	0.00	2.38	186.75	677.10	863.85	4.22
0.82	0.76	2.29	6.95	0.00	2.36	189.05	674.98	864.04	5.29
0.83	0.73	2.18	7.09	0.00	2.34	191.36	672.85	864.21	6.69
0.84	0.69	2.07	7.24	0.00	2.32	193.66	670.69	864.35	8.59
0.85	0.65	1.96	7.39	0.00	2.30	195.97	668.52	864.48	11.18
0.86	0.61	1.84	7.54	0.00	2.28	198.27	666.32	864.59	14.83
0.87	0.58	1.73	7.70	0.00	2.26	200.58	664.09	864.67	20.05
0.88	0.54	1.61	7.86	0.00	2.24	202.88	661.84	864.73	27.76
0.89	0.50	1.49	8.02	0.00	2.22	205.19	659.56	864.75	39.50
0.90	0.45	1.36	8.18	0.00	2.20	207.50	657.26	864.75	58.08
0.91	0.41	1.24	8.35	0.00	2.18	209.80	654.91	864.71	88.86
0.92	0.37	1.11	8.52	0.00	2.16	212.11	652.53	864.64	142.83
0.93	0.33	0.98	8.69	0.00	2.14	214.41	650.11	864.52	244.40
0.94	0.28	0.85	8.87	0.00	2.12	216.72	647.64	864.36	453.96
0.95	0.24	0.71	9.05	0.00	2.10	219.02	645.12	864.14	943.41

Figure 10: Entropy changes during the Haber process reaction at 10atm and 425K

Reacting Entities	Reactant 1	Reactant 2	Product 1	Product 2
Name	Nitrogen	Hydrogen	Ammonia	0
Stoichiometry	1	3	2	0
Standard molar entropy	192	131	192.45	0
Standard molar enthalpy	0.00	0.00	-46.11	0.00
Initial Amount (mol)	1	3	0	0
Initial partial pressures	2.5	7.5	0	0
xLN(x)	2.29	15.11	0.00	0.00

Reaction Conditions

Temperature (K)	425
Step size	0.01
Pressure	10.00

Initial Values

Extent of reaction	0.65
'Enthalpy'	-92.22
'Entropy'	-284.04

ξ	Pr1	Pr2	Pp1	Pp2	nt	Ssur	Ssys	Stot	"K"
0.65	1.30	3.89	4.81	0.00	2.70	141.04	708.92	849.96	0.30
0.66	1.27	3.81	4.93	0.00	2.68	143.21	707.02	850.24	0.35
0.67	1.24	3.72	5.04	0.00	2.66	145.38	705.12	850.50	0.40
0.68	1.21	3.64	5.15	0.00	2.64	147.55	703.20	850.75	0.46
0.69	1.18	3.55	5.27	0.00	2.62	149.72	701.27	851.00	0.52
0.70	1.15	3.46	5.38	0.00	2.60	151.89	699.33	851.23	0.61
0.71	1.12	3.37	5.50	0.00	2.58	154.06	697.38	851.44	0.70
0.72	1.09	3.28	5.63	0.00	2.56	156.23	695.42	851.65	0.82
0.73	1.06	3.19	5.75	0.00	2.54	158.40	693.44	851.84	0.96
0.74	1.03	3.10	5.87	0.00	2.52	160.57	691.45	852.02	1.13
0.75	1.00	3.00	6.00	0.00	2.50	162.74	689.44	852.19	1.33
0.76	0.97	2.90	6.13	0.00	2.48	164.91	687.43	852.34	1.59
0.77	0.93	2.80	6.26	0.00	2.46	167.08	685.39	852.47	1.90
0.78	0.90	2.70	6.39	0.00	2.44	169.25	683.34	852.60	2.29
0.79	0.87	2.60	6.53	0.00	2.42	171.42	681.28	852.70	2.78
0.80	0.83	2.50	6.67	0.00	2.40	173.59	679.20	852.79	3.41
0.81	0.80	2.39	6.81	0.00	2.38	175.76	677.10	852.86	4.22
0.82	0.76	2.29	6.95	0.00	2.36	177.93	674.98	852.91	5.29
0.83	0.73	2.18	7.09	0.00	2.34	180.10	672.85	852.95	6.69
0.84	0.69	2.07	7.24	0.00	2.32	182.27	670.69	852.96	8.59
0.85	0.65	1.96	7.39	0.00	2.30	184.44	668.52	852.96	11.18
0.86	0.61	1.84	7.54	0.00	2.28	186.61	666.32	852.93	14.83
0.87	0.58	1.73	7.70	0.00	2.26	188.78	664.09	852.87	20.05
0.88	0.54	1.61	7.86	0.00	2.24	190.95	661.84	852.79	27.76
0.89	0.50	1.49	8.02	0.00	2.22	193.12	659.56	852.68	39.50
0.90	0.45	1.36	8.18	0.00	2.20	195.29	657.26	852.54	58.08
0.91	0.41	1.24	8.35	0.00	2.18	197.46	654.91	852.37	88.86
0.92	0.37	1.11	8.52	0.00	2.16	199.63	652.53	852.16	142.83
0.93	0.33	0.98	8.69	0.00	2.14	201.80	650.11	851.91	244.40
0.94	0.28	0.85	8.87	0.00	2.12	203.97	647.64	851.61	453.96
0.95	0.24	0.71	9.05	0.00	2.10	206.14	645.12	851.26	943.41

Figure 11: Entropy changes during the Haber process reaction at 1atm and 400K

Reacting Entities	Reactant 1	Reactant 2	Product 1	Product 2
Name	Nitrogen	Hydrogen	Ammonia	0
Stoichiometry	1	3	2	0
Standard molar entropy	192	131	192.45	0
Standard molar enthalpy	0.00	0.00	-46.11	0.00
Initial Amount (mol)	1	3	0	0
Initial partial pressures	0.25	0.75	0	0
xLN(x)	-0.35	-0.22	0.00	0.00

Reaction Conditions

Temperature (K)	400
Step size	0.01
Pressure	1.00

Initial Values

Extent of reaction	0.65
'Enthalpy'	-92.22
'Entropy'	611.69

ξ	Pr1	Pr2	Pp1	Pp2	nt	Ssur	Ssys	Stot	"K"
0.65	0.13	0.39	0.48	0.00	2.70	149.86	-135.15	14.71	30.41
0.66	0.13	0.38	0.49	0.00	2.68	152.16	-137.42	14.74	34.68
0.67	0.12	0.37	0.50	0.00	2.66	154.47	-139.71	14.76	39.68
0.68	0.12	0.36	0.52	0.00	2.64	156.77	-142.01	14.76	45.53
0.69	0.12	0.35	0.53	0.00	2.62	159.08	-144.32	14.76	52.43
0.70	0.12	0.35	0.54	0.00	2.60	161.39	-146.64	14.74	60.58
0.71	0.11	0.34	0.55	0.00	2.58	163.69	-148.98	14.71	70.28
0.72	0.11	0.33	0.56	0.00	2.56	166.00	-151.33	14.67	81.89
0.73	0.11	0.32	0.57	0.00	2.54	168.30	-153.69	14.62	95.84
0.74	0.10	0.31	0.59	0.00	2.52	170.61	-156.06	14.55	112.74
0.75	0.10	0.30	0.60	0.00	2.50	172.91	-158.45	14.47	133.33
0.76	0.10	0.29	0.61	0.00	2.48	175.22	-160.85	14.37	158.63
0.77	0.09	0.28	0.63	0.00	2.46	177.52	-163.26	14.26	189.95
0.78	0.09	0.27	0.64	0.00	2.44	179.83	-165.69	14.13	229.07
0.79	0.09	0.26	0.65	0.00	2.42	182.13	-168.14	13.99	278.42
0.80	0.08	0.25	0.67	0.00	2.40	184.44	-170.60	13.84	341.33
0.81	0.08	0.24	0.68	0.00	2.38	186.75	-173.09	13.66	422.48
0.82	0.08	0.23	0.69	0.00	2.36	189.05	-175.59	13.47	528.52
0.83	0.07	0.22	0.71	0.00	2.34	191.36	-178.10	13.25	669.10
0.84	0.07	0.21	0.72	0.00	2.32	193.66	-180.64	13.02	858.52
0.85	0.07	0.20	0.74	0.00	2.30	195.97	-183.20	12.77	1118.47
0.86	0.06	0.18	0.75	0.00	2.28	198.27	-185.78	12.49	1482.69
0.87	0.06	0.17	0.77	0.00	2.26	200.58	-188.39	12.19	2005.29
0.88	0.05	0.16	0.79	0.00	2.24	202.88	-191.02	11.86	2776.08
0.89	0.05	0.15	0.80	0.00	2.22	205.19	-193.68	11.51	3950.13
0.90	0.05	0.14	0.82	0.00	2.20	207.50	-196.38	11.12	5808.00
0.91	0.04	0.12	0.83	0.00	2.18	209.80	-199.10	10.70	8886.32
0.92	0.04	0.11	0.85	0.00	2.16	212.11	-201.86	10.24	14283.00
0.93	0.03	0.10	0.87	0.00	2.14	214.41	-204.67	9.74	24439.79
0.94	0.03	0.08	0.89	0.00	2.12	216.72	-207.52	9.20	45396.11
0.95	0.02	0.07	0.90	0.00	2.10	219.02	-210.43	8.59	94341.33

The sheets shown in Figures 9, 10 and 11 were produced as follows:

1. The required thermodynamic data for the chosen reaction are entered in the 'reacting Entities' box at the top of the sheet together with the names of the reactant(s) and product(s) and their initial amounts. (The worksheet can deal with one or two reactants and one or two products.) These are used to calculate the mole fractions of each component that are initially present.
2. The user chooses the conditions to be investigated and enters the selected temperature and pressure in the 'Reaction Conditions' box. Additionally the extent of reaction that the sheet will start at and the size by which it will increase are entered in the 'Initial Values' and 'Reaction conditions' boxes respectively. These data are then used to calculate the derived thermodynamic variables in the columns below the boxes.
3. The first column contains the extent of reaction, ξ . The starting point of this can be set so that one region of the reaction - e.g. the area around the position of equilibrium - can be explored in detail without an enormous table to having to be produced.
4. The next four columns calculate the partial pressures of the reactants and products. In the case of the Haber process reaction there is only one product so the column Pp2 reads 0. The partial pressure of each component is equal to its mole fraction times the total pressure. The formulae used are:-

$$\text{Nitrogen: } P_t \cdot (1 - \xi) / (4 - 2 \cdot \xi)$$

$$\text{Hydrogen: } 3 \cdot P_t \cdot (1 - \xi) / (4 - 2 \cdot \xi) \text{ i.e. three times as large as that of nitrogen}$$

$$\text{Ammonia: } 2 \cdot P_t \cdot \xi / (4 - 2 \cdot \xi)$$

where ξ is the extent of reaction, and P_t the total pressure.

4. The 'nt' column calculates the total number of moles present - i.e. summing those initially present plus or minus those formed in the reaction. This value is used two columns later to calculate the entropy change in the system.
6. The next column calculates the entropy change in the surroundings at each step.

$$\text{The molar value is taken as: } \Delta S^\theta_{(\text{surr})} = -\Delta H^\theta / T$$

and other values are obtained by multiplying the molar value by the extent of reaction.

7. In the next column, the pressure, the partial pressures of each component, and the total number of moles present are used to calculate the entropy of the system using:

$$\Delta S = (nt/P_t) \cdot \sum (p_x \cdot S^\theta_x - R \cdot \ln p_x) -$$

where p_x is the partial pressure, and S^θ_x the standard molar entropy of each component

The entropies of the initial, unreacted, mixture of nitrogen and hydrogen (also corrected for the set total pressure and calculated in cell I15) are then subtracted to give the entropy change of the system.

8. The penultimate column contains the final value of the total entropy change at the given extent of reaction. It is just the sum of the previous two columns.

9. The final column calculates the ‘equilibrium constant’ at each extent of reaction. It can be seen that, the calculated and ‘real’ values are very close. Students often expect them to match exactly but this is rarely the case - mainly due, as mentioned earlier, to the great dependence of the calculated entropy maximum on the thermodynamic data. This is an excellent point to explore and discuss with students.

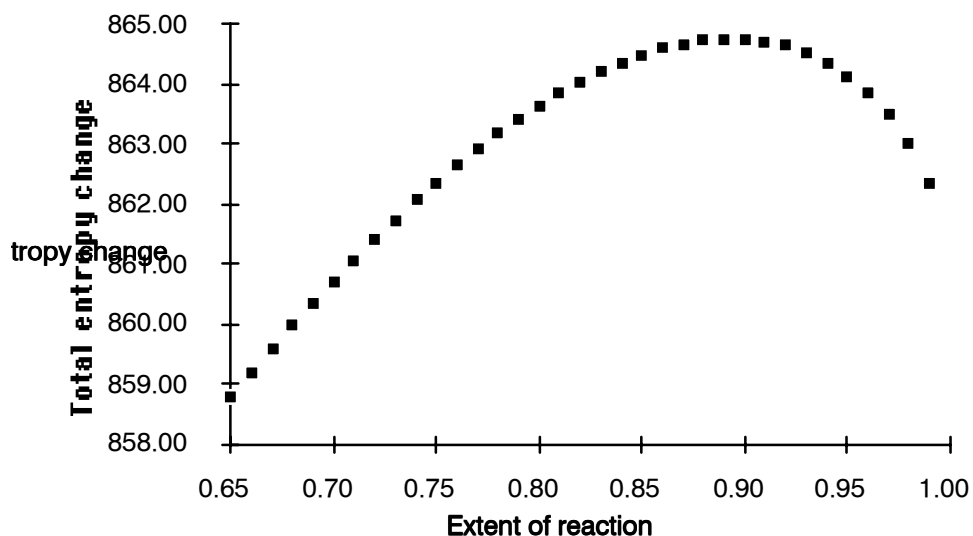
4.3 USING THE WORKSHEET

When the worksheet is used it is much easier for students to see the effects if they are shown graphically as well as in tabular form. The graphs give a feel of the overall ‘shape’ of the change and then the table can be used to investigate the values in more details. One further advantage of the graphical display is that it changes automatically as the conditions are altered.

4.3.1 THE INITIAL VALUES

If the suggested initial conditions are used with a starting extent of reaction of .65 then, as Figure 12 shows, a clear maximum is seen at about .9 extent of reaction. Although this is near the maximum extent of reaction, it provides a good starting value for the further explorations described below.

Figure 12: Entropy changes during the Haber process reaction at 10atm and 400K



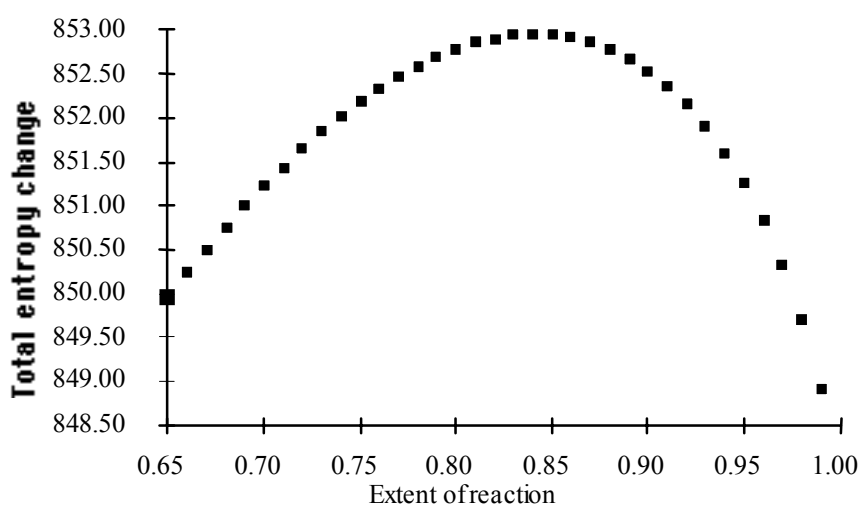
4.3.1 VARYING THE TEMPERATURE

It is useful to ask the students to use Le Chatelier’s principle to predict what effect varying the temperature will have before they change the conditions. When they do vary the temperature they will see that as it increases the position of equilibrium shifts towards the reactants. This is illustrated in Figure 13 and is of course exactly what as Le Chatelier’s principle predicts for exothermic reactions such as this. An increase of 25K corresponds to an extent of reaction of about .85. If the students examine the table they will see that the equilibrium constant has decreased - to a value of about 10. Most students do not find this unexpected since they assume that a change in the ‘position of

equilibrium' will necessitate a change in the equilibrium constant. However the point of getting the students to note the new value comes when they compare the effect of changing temperature with that of changing pressure - where the equilibrium constant does not change.

A further exercise for students is to get them to use the temperature to achieve a given extent of reaction or equilibrium constant. If they try this they can explore whether the same change in temperature always has the same absolute or proportional effect on either ΔS_{tot} or K .

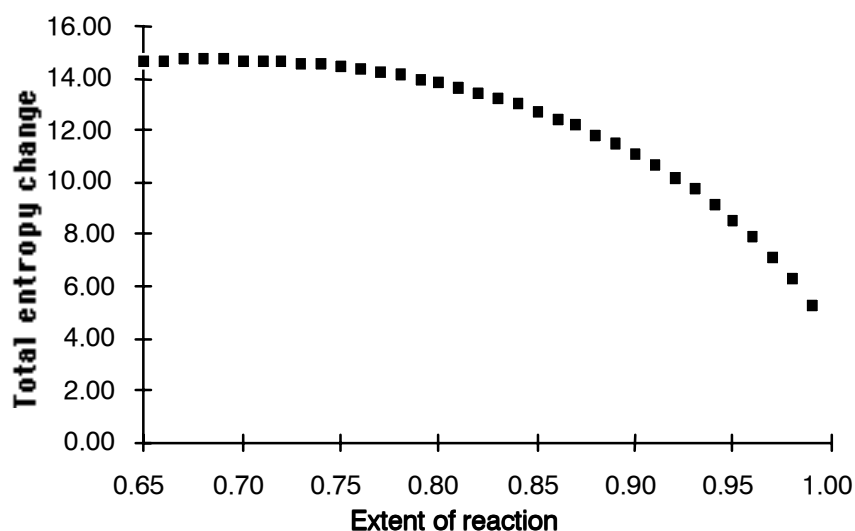
Figure 13: Entropy changes during the Haber process reaction at 10atm and 425K



4.3.3 VARYING THE PRESSURE

Again it is best to ask student to predict how the composition of the equilibrium mixture will vary as the pressure is varied and then use the worksheet to confirm that it does so in the way Le Chatelier's principle predicts. Figure 14 shows the result obtained.

Figure 14: Entropy changes during the Haber process reaction at 10atm and 400K



The key point of this exercise is when the students examine the equilibrium constant at the new entropy maximum. They are usually surprised to see that it is the same K value as at the higher pressure (and the same temperature). Their difficulty lies in understanding how at two pressures the 'position of equilibrium' can be different but the equilibrium constant the same. The worksheet allows this phenomenon to be seen in a simple and striking way and should provide a good basis for further discussion and exploration.

5. THE EXAMPLES - MONTE CARLO MODEL OF EQUILIBRIUM

Monte Carlo or probabilistic modelling has many advantages, perhaps the greatest of which is that it accurately reflects and makes explicit the causal character of chemical reactions in that it is probabilistic at the micro level and deterministic at the macro level. Unfortunately most models are complex - both to programme and to run. Here a spreadsheet is used to produce a basic Monte Carlo type model of the simple chemical equilibrium:



Conceptually Monte Carlo modelling is an extension of the probabilistic interpretation of entropy. However the look of the model and the kind of ideas used to explain it are so different from those used in the previous section that the link is not obvious to many students. Maybe this model is best discussed **before** the more mathematical treatment described in section 4 and could serve as an introduction to it.

5.1 THE MODEL

The screen display (see Figure 15 shows the 'reaction box' within which one enters the chosen initial amounts of reactant and product. The probabilities of the forward and reverse reactions are then entered. These represent the chance that a randomly selected molecule of reactant or product has the correct energy, orientation, and energy distribution to react on collision. Any initial amounts of reactant and product may be chosen as may any reaction probability between 0 and 1.

Figure 15: The Monte Carlo Model.

b	b	b	a	b	b	b	b
a	b	a	b	b	a	b	a
b	b	a	b	b	b	b	b
a	b	b	a	b	b	b	a
b	a	b	b	b	b	b	a
b	b	b	b	b	b	a	a
b	b	b	b	a	b	b	a
b	b	a	b	a	b	b	b
a	b	b	b	b	b	b	a
a	b	b	a	a	b	b	b

Probability of Forward Reaction

Probability of Reverse Reaction

The model is controlled by a command macro⁶, (an annotated listing of which is shown in Table 5 in the Appendix). When the model is run, a cell within the 'reaction box' is selected at random. A random number between 0 - 1 is generated and if this is higher than the probability of reaction for the species chosen, the reaction takes place. When successful reaction happens, the computer 'beeps', giving an audible indication of the

rate of reaction. This process repeats until the machine is told to stop. After every 20 attempts the concentrations of reactant and product are recalculated and a value for 'K' determined.

5.2 CLASSROOM USE

The model allows a number of important points to be made about chemical equilibria and the rates of reactions in addition to the central question of causality. These concern both the rate of the reaction and the equilibrium concentrations:

a. The **rate of the reactions** is determined by:-

1. the concentrations not the amounts. This can be shown by adapting the macro to use a smaller 'box' (say 5x5) full of reactants, running the model and then putting the same amount of reactants in the larger 'box'. The rate of reaction will be slower in the second case. As the system only recognises the symbols "a" and "b" the empty can be filled with another symbol (or left blank) to indicate the solvent molecules.
2. the sizes of the probabilities of reaction. These correspond to colliding molecules having the correct energy, orientation etc. They can therefore be correlated with work on activation energies, particularly the Maxwell-Boltzmann distribution.

b. The **equilibrium concentrations**:-

1. depend on the ratio of the probabilities of reaction. This can be explored using different probabilities of reaction and the equilibrium relationship

$$K = [b]/[a] = (\text{Probability of forward reaction})/(\text{Probability of back reaction})$$

can be determined. Another way of expressing this is to say that at equilibrium there must be more of the species which is less likely to react so that the chances of either reaction being successful are the same. i.e. (Probability of forward reaction)*[a] = (Probability of back reaction)*[b]

2. are not the same unless the probabilities of reaction are the same. This follows from the point above but is worth stressing as there is evidence⁷ that many students believe that equilibrium concentrations of reactants and products are either similar or in the ratio of the stoichiometry of the reaction.
3. do not depend on the initial amounts or concentrations of reactants and products. The idea that they do is easily shown to be false by running the reaction with different initial amounts of reactant and product.
4. are not static but vary around the mean ratio given by the equilibrium constant. The key point here is to demonstrate that the equilibrium is dynamic. After a while the overall rate of reaction will be very slow - the concentrations will not vary much - but both the forward and reverse reactions will still be taking place.
5. fluctuate by smaller percentages as the amounts of reactant and product increase. This is the key idea in explaining how we can be deterministic about probabilistic processes. Boxes of different sizes can be used to explore the relative size of the

fluctuations and see that as the size of the system increases we can be more sure about the concentrations present at equilibrium - they fluctuate by a smaller percentage. It might then be appreciated that were the box to be big enough to contain amounts that one might normally react (say $10^{13} \times 10^{13}$!) then the relative size of these fluctuations would be so small as to be undetectable.

The implications of the model can be explored through a teacher demonstration but is best suited for use by small groups of students - allowing groups to explore aspects of the model using exercises based on the suggestions given above and following this with a class discussion of their results.

APPENDIX

Table 1: Formulae needed to construct the worksheet shown in Figure 2

Box	Contents
B10	$B10 - B6 * B1$
B12	$B8 + B10$
E15	$(E12^{E6}) * (F12^{B6}) / ((B12^{B6}) * (C12^{C6}))$
B15	$LN(B15)$

Table 2: Macro-sheet used in modelling the acid-base titration (Figure 5)

Titrate
=ARGUMENT("Ca")
=ARGUMENT("Cb")
=ARGUMENT("Ka")
=ARGUMENT("Kb")
=ARGUMENT("Va")
=ARGUMENT("Kw")
=ARGUMENT("H")
=ARGUMENT("MErr")
=ARGUMENT("Vb")
=ARGUMENT("Vf")
=SET.NAME("fH", Vf+Cb*Vb/((Kw/Kb)+H) -Vf*Kw/(H^2)-Ka*Ca*Va/(H*(Ka+H)))
=SET.NAME("dH", -Cb*Vb/(((Kw/Kb)+H)^2) +2*Vf*Kw/(H^3)+Ka*Ca*Va*(Ka+2*H)/((H*(Ka+H))^2))
=H
=fH/dH
=IF((H>ABS(fH/dH)),GOTO(A19))
=SET.NAME("fH", fH/2)
=GOTO(A15)
=IF(ABS(fH/dH)<MErr,RETURN(H))
=SET.NAME("H", H-(fH/dH))
=IF(H>Ca,SET.NAME("H",0.000000000000001))
=GOTO(A12)

Table 3: Formulae needed to construct the worksheet shown in Figure 6

Cell	Contents
A4 (the [A] column)	$A3 - C3 + F3$
C4 the d[A] column)	$A4 * B4$
D4 the [B] column)	$D3 - F3 + C3$
F4 the d[B] column)	$E4 * D4$

Table 4: Formulae needed to construct the worksheets shown in Figures 9, 10 and 11

Cell	Contents
E9	$\$E\$8*\$D\$15/SUM(\$E\$8:\$K\$8)$
E10	$IF(E9>0,E9*LN(E9),0)$
I14	$\$I\$7*\$I\$5+\$K\$7*\$K\$5-\$E\$7*\$E\$5-\$G\$7*\$G\5
I15	$((\$E\$8*\$E\$6+\$G\$8*\$G\$6+\$I\$8*\$I\$6+\$K\$8*\$K\$6)-$ $(SUM(\$E\$5:\$K\$5))*8.31*(SUM(\$E\$10:\$K\$10)))$
B18	$\$I\13
B19	$B18+\$D\14
C19	$(\$E\$8-\$E\$5*B19)*\$D\$15/G19$
G19	$(\$E\$8-\$E\$5*B19)+(\$G\$8-\$G\$5*B19)+(\$I\$8+\$I\$5*B19)+(\$K\$8+\$K\$5*B19)$
H19	$-B19*1000*\$I\$14/\$D\13
I19	$(G19/\$D\$15)*((C19*\$E\$6+D19*\$G\$6+E19*\$I\$6+F19*\$K\$6)-$ $8.31*(IF(C19>0,C19*LN(C19),0)+IF(D19>0,D19*LN(D19),0)+$ $IF(E19>0,E19*LN(E19),0)+IF(F19>0,F19*LN(F19),0)))-\$I\$15$
J19	$H19+I19$
K19	$(IF(E19=0,1,(E19^\$I\$5))*IF(F19=0,1,(F19^\$K\$5)))/$ $(IF(C19=0,1,(C19^\$E\$5))*IF(D19=0,1,(D19^\$G\$5)))$

NOTE:

1. Cells D19 to F19 are filled by copying across the contents of cell C19.
2. The 'IF' statements in cells I19 and K19 are to cope with the fact that only one reactant or product may be present. They stop the spreadsheet trying to calculate the value of LN(0) or raising 0 to a power - both of which would cause problems!

Table 5: Macro sheet for the Monte Carlo Model (Figure 15)

Initial count
=SET.NAME("Re",0)
=SET.NAME("Pr",0)
=SELECT(!A3)
=FOR("count1",1,10,1)
=FOR("count2",1,10,1)
=SELECT("RC[1]")
=ACTIVE.CELL()
=IF(A8="a",SET.NAME("Re",Re+1),SET.NAME("Pr",Pr+1))
=NEXT()
=SELECT("R[1]C[-10]")
=NEXT()
=RUN(Macro!reaction)
reaction
=SET.NAME("pf",!H14)
=SET.NAME("pb",!H16)
=RUN(Macro!update)
=FOR("counter",1,20,1)
=SET.NAME("x",INT(10*RAND()))
=SET.NAME("y",INT(10*RAND()))
=SET.NAME("cell",OFFSET(!B\$3,y,x))
=cell
=SELECT(cell)
=IF(AND(pf>RAND(),A22="a"),RUN(Macro!prod),
IF(AND(pb>RAND(),A22="b"),RUN(Macro!react),GOTO(A26)))
=BEEP()
=NEXT()
=GOTO(A17)
=RETURN()
prod
=FORMULA("b")
=SET.NAME("Re",Re-1)
=SET.NAME("Pr",Pr+1)
=RETURN()
react
=FORMULA("a")
=SET.NAME("Re",Re+1)
=SET.NAME("Pr",Pr-1)
=RETURN()
update screen
=SELECT(!K\$14)
=FORMULA(Re/100)
=SELECT(!K\$15)
=FORMULA(Pr/100)
=SELECT(!K\$16)
=IF(Re=0,FORMULA(0),FORMULA(Pr/Re))
=RETURN()

REFERENCES

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