Some calculations for organic chemists: boiling point variation, Boltzmann factors and the Eyring equation

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Abstract

How do the boiling points of substances vary with pressure? Commonly used nomographs can give a misleading impression of accuracy. An applet is presented which gives a more precise measure of the uncertainty in the calculation, whilst giving a straightforward way to calculate how boiling points may vary with pressure. Related applets calculate Boltzmann factors and the solution to the Eyring equation, which give an idea of how rate and selectivity may change with temperature. © 2000 Elsevier Science Ltd. All rights reserved.

How can the boiling point of a substance at reduced pressure be estimated, knowing only the boiling point under one atmosphere (or some other pressure)? This calculation is frequently required in chemistry laboratories, but the approximations and uncertainties involved are complex. A printed nomograph is often used, but this cannot hold all of the information that it would be useful to convey. This paper presents a method to: (i) provide a straightforward way to obtain a quantitative estimate of a boiling point at reduced pressure, (ii) provide a quantitative estimate of the uncertainty in the measurement, (iii) use the T-H-E rule, rather than the simpler Trouton's Law method of estimating boiling point variation (this is not possible with a normal printed nomograph), and (iv) provide routines to calculate Boltzmann factors and the solution to the Eyring equation.

The use of this procedure gives a more reliable method of estimating boiling points at reduced pressure. This both reduces the likelihood of a volatile compound being accidentally sucked into a pump and also increases the degree of certainty with which this possible explanation for a low or zero yield may be accepted or discounted.

For many chemistry-related calculations, a graph may be a suitable way of providing an approximate numerical answer to a calculation. For example, Boltzmann factors are often used to calculate the energy difference between two states, given a ratio, in thermodynamic equi-

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librium, at a particular temperature, or to calculate an expected ratio given an energy difference. It would be more useful to have a three-dimensional graph, as this would give the relationship at any temperature. Alternatively, the calculation can be done on a computer, provided the program that does this can run on a computer cheap enough to risk having near a laboratory. The Java programming language[1] provides a strategy for doing this, as it can create programs that run within a web browser. A Java applet which calculates Boltzmann factors,[2] is available on: http://www.ch.cam.ac.uk/magnus/boltz.html. It is possible to switch between logarithmic and linear scales, making the line straight or curved, respectively.

$$\text{Ratio} = \exp\left(\frac{-\Delta E}{RT}\right) \tag{1}$$

Boltzmann factors: the ratio of two states, related to the energy difference (ΔE) between them and the temperature in Kelvin. R is the gas constant.

Another commonly used expression is the Eyring equation, which can be used to estimate rate constants from their free energy of activation. This is particularly useful for conformational transitions.[3] A slightly more complicated calculation is required to interpret the Eyring equation (Eq. (2)). In this case neither a linear nor logarithmic plot will be a straight line, and so a printed graph is harder to use. In addition, since T appears twice in the equation, it is not straightforward to work out the temperature that corresponds to particular values of k and $\Delta G^{\ddagger}$. This is not a problem for the computer, and an applet that performs the calculations is available on the URL: http://www.ch.cam.ac.uk/magnus/eyring.html.

$$k = \left(\frac{k_{B}T}{h}\right) \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \tag{2}$$

Eyring equation, an approximation for a rate constant, k, at temperature T, with a free energy of activation $\Delta G^{\ddagger}$. The Boltzmann constant is k_{B} and h is Planck's constant.

Calculating boiling point changes is a qualitatively different problem, as the equations used are approximate, and so a measure of the uncertainty in the result is required as well as a numeric answer. Boiling points decrease with pressure, and nomographs provide a very useful guide, but can be misleading. The variation of boiling point with pressure follows the Clausius–Clapeyron equation (Eq. (3)):[2]

$$\frac{\text{d}\ln(p)}{\text{d}T} = \frac{\Delta_{vap}H}{RT^{2}} \tag{3}$$

Clausius–Clapeyron equation: p is the pressure, $\Delta_{vap}H$ is the enthalpy of vapourisation, R is the gas constant and T is the temperature in Kelvin.

If we assume that $\Delta_{vap}H$ is constant, this can be integrated to give (Eq. (4)) where p^{*} and T^{*} are the pressure and temperature at one boiling point of the substance of interest. This equation gives a relationship between boiling point and pressure, provided that $\Delta_{vap}H$ is constant and its value is known.

$$\ln \frac{p}{p*} = \frac{-\Delta_{\mathrm{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T*}\right) \tag{4}$$

Integration of the Clausius–Clapeyron equation.

Values for $\Delta_{\mathrm{vap}}H$ are available for a range of compounds,[2] but it is empirically observed that the entropy of vapourisation, which is equal to the enthalpy of vapourisation divided by the temperature of vapourisation, is usually equal to 85 J K^{-1} mol^{-1}. This is known as Trouton's rule (Eq. (5)).[4,5]

$$\Delta_{\mathrm{vap}}S = \frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{b}}} = 85 \text{ J K}^{-1} \text{ mol}^{-1} \tag{5}$$

Trouton's rule: T_{b} is the boiling point at atmospheric pressure.

With this piece of information, it is possible to construct a graph that relates pressure and temperature. However, the entropy of vapourisation of water is 109 J K^{-1} mol^{-1} and the entropy of vapourisation of methane is 73 J K^{-1} mol^{-1}. These different values can lead to very different estimates of the temperature variation of boiling points with pressure (Fig. 1). The program marks lines for both water and methane, as well as a Trouton line. If the boiling point is known only at a pressure other than atmospheric pressure, then the same equation can be used to obtain an estimate for the boiling point at atmospheric pressure. This can then be used to calculate boiling points at other pressures.
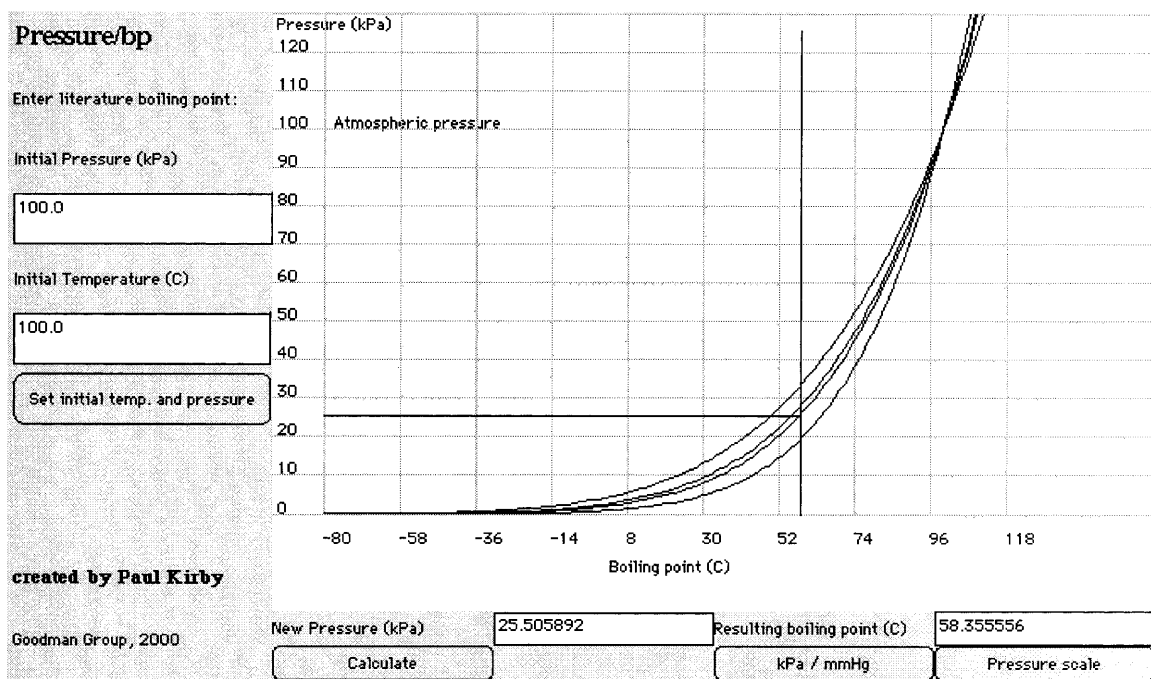

Figure 1. The variation of boiling point with pressure, giving an indication of uncertainty

The solutions to the equations are given by a Java applet which is available on the URL: http://www.ch.cam.ac.uk/magnus/boil.html and is illustrated in Fig. 1. The boiling point of a substance at atmospheric pressure is entered into the box on the top left of the applet. The graph

will then show three lines. The central one is for Trouton's rule, the upper one for water with an entropy of vapourisation of 109 J K^{-1} mol^{-1}, and the lower one for methane, with an entropy of vapourisation of 73 J K^{-1} mol^{-1}. Clicking anywhere on the graph will give a boiling point at the pressure selected. This rapidly gives an estimate of how boiling point changes with pressure, and also allows a qualitative estimate of the accuracy of the calculation. Is the substance of interest more like water or more like methane? The readings are available from the graph.

A slightly better rule is available, the Trouton–Hildebrand–Everett rule or T-H-E rule.[6,7] The entropy of vapourisation is set not to 85 J K^{-1} mol^{-1} but to $R(4.4+\ln T_b)$ where T_b is the boiling point at atmospheric pressure and R is the gas constant (Eq. (6)). This small correction is too complicated to be included in a general printed nomograph, but can easily be incorporated into the applet. If the reference boiling point is given at atmospheric pressure, then applet automatically plots the T-H-E rule line, in green. If the reference pressure is not atmospheric, then the applet uses the T-H-E rule to estimate the boiling point at atmospheric pressure. In these cases, the green line is omitted to indicate that the calculation may be less accurate.

$$\frac{\Delta H_{vap}}{RT_b} = (4.4+\ln T_b) \tag{6}$$

Trouton–Hildebrand–Everett rule: T_b, is numeric value of the boiling point of the substance at atmospheric pressure expressed in Kelvin.

Acknowledgements

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