

AN INTRODUCTION TO THE BOLTZMANN FACTOR BY USING INFORMATION TECHNOLOGY TOOLS

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Abstract

We present an experiment and simulations aimed at introducing the Boltzmann factor mathematical expression and at illustrating the fundamental concepts on which it is grounded. The experiment uses an easily available Microcomputer Based Laboratory apparatus. Simulations are developed in the Net-Logo environment that, besides having a friendly user-interface, allows an easy interaction with the algorithm. The approach supplies a pedagogical support for the introduction of the Boltzmann factor at undergraduate level to students without a background in statistical mechanics.

1. Introduction

One of the main objectives of Science is to supply an unifying framework for the description and interpretation of phenomena developing in different fields. In physics, the Boltzmann factor (B-

factor), $e^{-\frac{E_i}{kT}}$, is at the basis of the description of a great amount of systems, both classical and quantum. For a system of particles at a given temperature, T , it represents the fraction F_i of particles with energy E_i .

To understand why the B-factor has its specific form involves a mathematical analysis whose flow of logic is hard to see and that is not always at the level of high school or college students' preparation. Books for undergraduate students use different approaches and arguments for its derivation: most of them, following Feynman (Feynman et al., 1963), justify it heuristically by referring to the "exponential atmosphere", others analyse the quasi-continuous states of the heat bath (Feynman, 1974; Reif, 1965) or use the method of the most probable distribution (Schrödinger, 1967).

Some pedagogical experiments directly related to the B-factor have been published, as that suggested by Einstein and first performed by Perrin (Perrin, 1909): the sedimentation equilibrium of colloidal suspensions. The experiment analyses the behaviour of small plastic spheres suspended in a liquid slightly denser than water representing a miniature atmosphere (Horne, 1973). The measure of the sphere concentration at different heights obeys an exponential law, according to the Boltzmann factor.

In a previous paper (Battaglia et al., 2009) we described experiments analysing thermodynamic and electric phenomena and introduced an analogical mechanical model able to interpret the experimental results in different fields of physics, highlighting the physical meaning of the B-factor. In this paper, we present an alternative experiment, based on the study of the speed of a chemical reaction as a function of the reactant temperature and propose a working model able to make sense of the experimental results and its implementation. The conclusion outlines the main features of the approach and its pedagogical relevance.

2. The experiment

The chemical reaction we use here to study the temperature dependence of its speed is a classical one, called the "formaldehyde clock reaction". It consists in the mixing of two clear solutions (solution A and B). At first there is no visible reaction, but after a short time delay, the liquid suddenly turns to a shade of pink, showing that a reaction has developed during a time interval that can be easily monitored.

Solution A consists of sodium disulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium sulfite (Na_2SO_3) dissolved in water¹; solution B consists of formaldehyde (HCHO) and phenolphthalein ($\text{C}_{20}\text{H}_{14}\text{O}_4$), also mixed with water². After dissolving in water, solution A mainly contains bisulfite (HSO_3^-), sulfite (SO_3^{2-}) and

¹ 5g of anhydrous $\text{Na}_2\text{S}_2\text{O}_5$ and 1g of anhydrous Na_2SO_3 in 1 liter of water.

² 10 cm³ of commercial 37% HCHO solution (water-10% methyl alcohol) in 1 liter of water.

sodium (Na^+) ions. In solution B, formaldehyde is almost completely hydrated to methylene glycol ($\text{CH}_2(\text{OH})_2$), with only about 0.1% free formaldehyde left (Burnett, 1982).

When solution A is mixed with solution B, a reaction develops between the SO_3^- ions and the free HCHO , that can be represented by the following reaction:



Reaction (1) releases hydroxide ions (OH^-) that would turn the phenolphthalein pink but they are quickly captured by bisulfite ions in the following reaction



So, as long as reaction (2) develops, the solution mixture stays transparent. Once, after a time Δt , all the HSO_3^- ions have been exhausted, OH^- ions can no longer be removed, and the phenolphthalein can turn pink, marking the conclusion of reaction (2).

A possible method to study the temperature dependence of the formaldehyde reaction speed is to measure Δt with a chronometer, spotting the instant reaction (2) ends by visually finding the instant the mixture color changes. In order to minimize the uncertainty arising from this last method, we here use a modified technique, detecting the exact instant in which the phenolphthalein starts turning pink by studying the mixture light absorbance with a microcomputer based spectrometer.

The experimental apparatus is shown in Fig. 1 and consists of a transparent glass cylinder, containing 100 ml of solution A, placed in a large glass container filled with water, whose temperature can be controlled by a thermoregulator. An optic fiber is placed inside the cylinder, together with a semiconductor temperature probe that monitors the solution's temperature. A white light source is placed near the container, as shown in Fig. 1. Solution B (100 ml) is placed in another cylinder, where it reaches an equilibrium temperature with the thermal bath. By means of the spectrometer, we study the light absorbance of the mixture from the instant at which solution B is mixed with solution A.

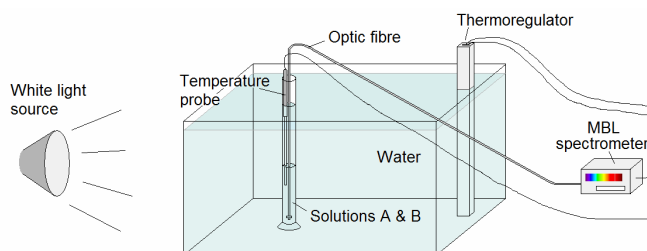
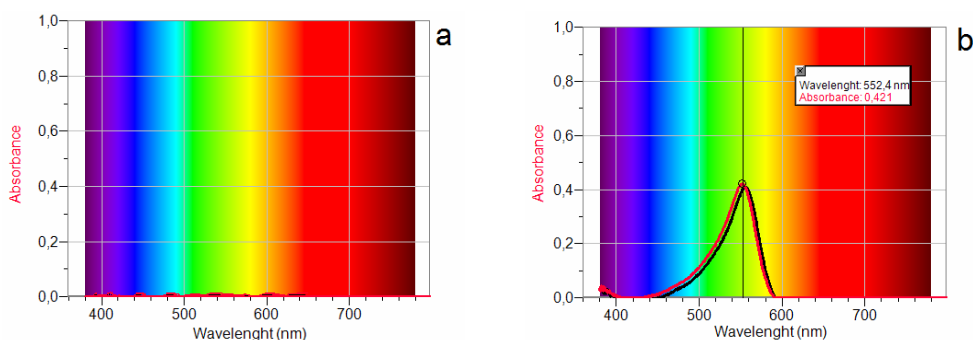


Fig. 1. The experimental apparatus.

In order to determine the exact wavelength of light for the absorbance measurements, we first study the solution A & B absorbance as a function of light wavelength during the reaction, at a given temperature. Our results are represented in Figs. 7a and 7b, that report an example of the collected absorbance spectra during reaction (2) and after its end, respectively.



Figs 2a and 2b. Spectra of light absorbance of solutions A&B before (a) and after (b) reaction (2) has ended ($T = 294 \text{ K}$).

As it easy to see, the spectrum is almost flat during the development of reaction (2) (i.e., no light is absorbed), while it shows a peak at a given wavelength (about 552 nm) when the reaction has ended and the phenolphthalein reacts with OH^- ions, turning pink. Absorbance as a function of wavelength measurements are repeated several times and also at different temperatures, and no appreciable deviation of the peak wavelength from the previously reported value is found.

We, then monitor the speed of reaction (2) by studying the absorbance of solutions A & B at 552 nm as a function of time. At each temperature value, the exact duration of the reaction is calculated by taking the time interval between the signal onset (i.e. when solution B is poured into solution A) and the instant at which the abrupt increase of the absorbance at 552 nm is detected by the sensor, marking the instant at which the two solution mixture starts to turn pink. Figure 3 shows some of the obtained results, from which it is evident that at a given temperature (294 K) the main reaction lasts more than in the case of a higher temperature (315 K).

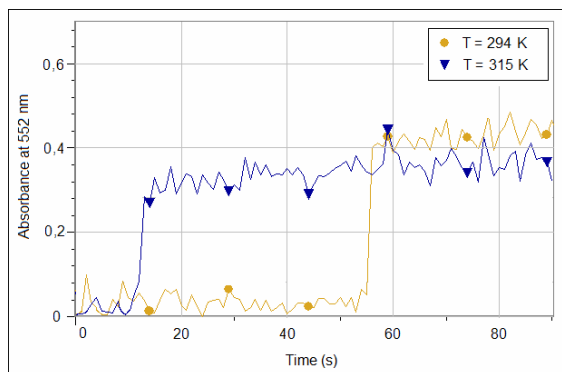


Figure 3. Absorbance of solutions A & B at 552 nm versus time at two different temperature values.

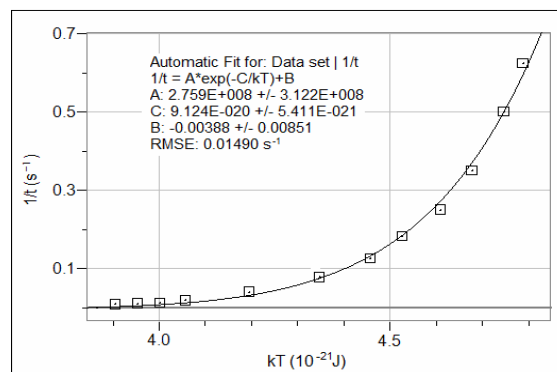


Figure 4. Speed of reaction versus kT with fitting curve.

Each measurement at a given temperature is repeated five times and average values are taken. Figure 4 reports the reciprocal of the measured time intervals (that is proportional to the speed of reaction) as a function of kT for the whole range of temperatures (282 K – 346 K) we studied. An exponential function is fitted to data and the fitting parameters are reported in figure.

Our experimental results and the data fitting show a clear exponential dependence of the speed of reaction on the reciprocal of temperature. This is in accordance with the well known Arrhenius equation, that expresses the dependence of the reaction speed, V , on the reactant temperature, T :

$$V = Ae^{-\frac{E_a}{kT}} \quad (4)$$

Here, A is a reaction-specific constant, k is the Boltzmann constant and E_a is the “activation energy” of the reaction. V has the units s^{-1} and it is often called the *reaction rate constant*.

According to the fit results, the activation energy of the formaldehyde clock reaction is equal to $(9.1 \pm 0.5) 10^{-20}$ J per molecule. This reaction has been widely studied and it is well known that the speed in the reaction of sulfite with formaldehyde in aqueous sulphite-bisulfite solution depends on the rate of the slowest of its steps, i.e. the dehydration of methylene glycol, that has to return in the pure formaldehyde form to react in (1) (Burnett, 1982; Winkelman, 2000). Values of the activation energy for the process have been estimated (Cassen, 1976; Winkelman, 2000) **Errore. Il segnalibro non è definito.** and are in good accordance with the value we found.

3. Model and simulations

The experiment deals with a situation where equilibrium conditions can be described on the basis of a simple two-level system (reactant mean kinetic energy less or more than the reaction activation energy), in which the B-factor appears in the evaluation of the temperature effect on the speed at which the two-levels are populated. A chemical reaction can develop only when the reactant molecules collide and, in order that the collision between two molecules, A and B, be effective for the reaction development, two conditions have to be fulfilled:

- A and B must possess a sufficient average energy (energy factor)
- A and B must collide with the appropriate reciprocal orientation (steric factor)

If the reactant concentration is constant, the reaction speed only depends on the fraction of effective collisions per time unit, i.e., neglecting the steric factor, on the fraction of reactant molecules per time unit having an average kinetic energy higher than the activation energy, E_a , typical of the specific reaction. At an absolute temperature T , the fraction of molecules that have a

kinetic energy greater than E_a can be calculated from the Maxwell-Boltzmann distribution and turns out to be proportional to the Boltzmann factor, $e^{-\frac{E_a}{kT}}$.

In order to understand the role of thermal energy in the onset of the analysed process, a mechanical model of a two-level system is developed and implemented through a simulation. It supplies a clear view of the dynamics of a mechanical two-level system and works by analogy with respect to the performed experiment.

The model system consists of a box containing some small hard spheres free of moving (see Fig. 5). The whole system friction is negligible and the spheres can interact among them and with the box walls through elastic collisions. The box floor consists of two equal parts at different levels, with a height difference h through a slope. Each sphere of mass m is free of moving from one level to the other one if its kinetic energy is enough to supply the necessary potential energy mgh .

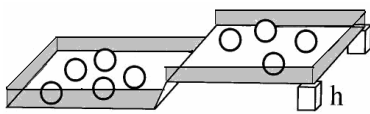


Figure 5. Mechanical model of a two-level system.

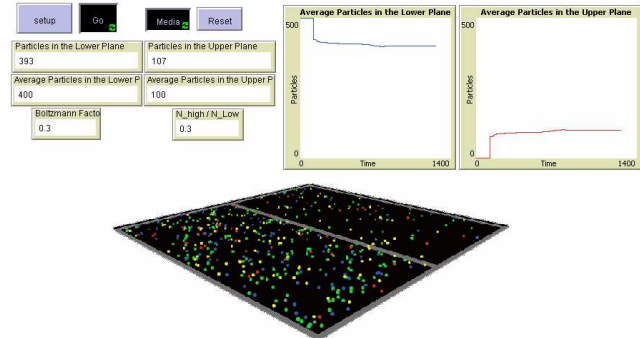
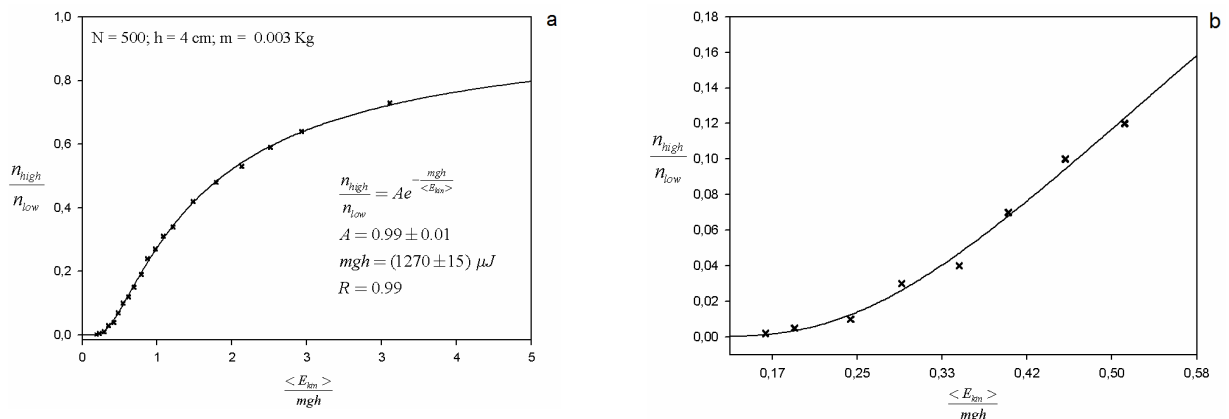


Figure 6. Net-Logo interface of the two-level mechanical system simulation.

The model implementation considers N spheres randomly distributed on the box floor, with the initial vector velocities equal in modulus and at random horizontal directions. Molecular dynamics is used for the numerical resolution of the equations of motion. After each collision, the new components of each sphere velocity are found by applying the laws of energy and momentum conservation. The program registers the number of particles for each level as a function of time.

Figure 6 shows the simulation interface implemented by using the Net-Logo environment (NetLogo, 2009). Different experiments with the model can be performed by varying the h values, the number of spheres and their initial velocity (and consequently the mean kinetic energy).

Some simulation results, obtained by varying the mean kinetic energy per particle $\langle E_{kin} \rangle$, are shown in figures 7 and 8. The reported simulations are performed with $N = 500$ hard spheres, with mean kinetic energy per particle in the range $0 < E_{kin} < 4mgh$. For all the simulations, the program is run until the fluctuations of the two population ratio, n_{high}/n_{low} , are almost constant.



Figures 7a and 7b. a) Simulation results of population ratio, n_{high}/n_{low} as a function of the ratio $\langle E_{kin} \rangle/mgh$. b) Enlargement of the initial part of figure 7

As shown in figures 7a and 7b, the dependence of n_{high}/n_{low} on the B-factor is evident, as well as its meaning. The ratio n_{high}/n_{low} varies from 0 to 1 as a function of the ratio $\langle E_{kin} \rangle/mgh$. When this ratio is high (low h or high kinetic energy) the particles do not “see” the change of energy level; for low

values of the ratio $\langle E_{kin} \rangle / mgh$ (high h or low kinetic energy), the population ratio increases at a higher rate. This is the case reported in our experiments.

The modelling of our experimental systems by means of a two-level system supplies, in our opinion, a twofold advantage: it presents an enlightening illustration of the argument and allows students to become familiar with a model widely used in physics for the description of simple systems of non-interacting particles, as dissociation of particles in liquids, spins in magnetic fields, and many others. All are examples of activation processes, in which for something to happen particles have to acquire an activation energy greater than kT . The higher the temperature, the more likely this is to occur. However, a small fraction of particles acquires a much larger than average energy and activates the process. The two-level model makes evident that “the activation energy is like a hill over which the particle has to climb before getting down into the next valley” (Ogborn, 2008).

4. Conclusion

The present approach shows how the B-factor can describe the experimental results in a typical example of chemical reaction. Other experiments can be performed, since many natural systems exist in two different states characterised by a transition gap ΔE . Examples include the evaporation of a liquid, where ΔE is the mean energy to supply a molecule to achieve the liquid-vapor transition, or the analysis of semiconductor behavior, where ΔE is the energy gap between valence and conduction bands. All such systems must borrow from their environment the necessary energy in order to change their state. The conceptual relevance of the dimensionless parameter $\Delta E/kT$, relies on the idea of the necessary balance between the energy needed for a process and the available energy.

The simulation illustrates a working model of a two-state atomic system. It can be improved by, for example, putting it in a temperature bath and requiring that the mean kinetic energy of both the two subsystems is maintained constant. It can be also extended to a multi-level system by allowing an easy visualization of the density distribution of atmosphere.

The reported experimental data have been collected during the physics lab section activities of the Physics Program of the Graduate School for Pre-Service Physics Teacher Education at Palermo University. The same approach has also been used during the lab activities of a Introductory Course of Statistical Mechanics for undergraduate engineering students. In both cases we found that the lack of a background in basic statistical mechanics did not prevent students to understand the explanations and argument. The experiments performed and the discussions about the simulation model, with its possible extensions, allow us to conclude that trainee teachers, as well as undergraduate students, have deepened their understanding of the physics content involved.

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