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Estimation Of Boltzmann Constant Using A Computer-Based Laboratory



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ABSTRACT

This work describes a simple method for estimating Boltzmann constant using a computer-based data acquisition system. This procedure consists of measuring the volume and pressure of hydrogen gas obtained through the electrolysis of water during a known time interval. The electrical charge is calculated by the software in real-time from the collection of data current as a function of time. This laboratory experiment is fast and sufficiently accurate to estimate Boltzmann constant, in which the percentage error was approximately 0.3 % of the accepted value. Discussion of the experimental procedure and the results obtained for different trials are presented. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Boltzmann constant;
Hoffmann electrolysis
apparatus;
Computer-based laboratory.

INTRODUCTION

The determination of Boltzmann constant k accurately is of great importance in teaching and understanding of physics and chemistry. The techniques which offer the best prospects for determining k are: The P-V-T gas thermometry, the acoustic gas thermometry, the radiometric determination of Stefan-Boltzmann constant, the measurement of the

electronic noise in a resistor and the measurement of Doppler broadening of a molecular absorption line^[1]. In this experiment, Boltzmann constant was determined from the P-V-T (Pressure-Volume-Temperature) gas thermometry, on the other hand from the ideal gas law.

This computer-based laboratory system was an extended version of the investigation done by Brittney Hoffman et al.^[2]. Our experiment was using

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Science Workshop 750 interface, Datastudio software and current sensor of PASCO^[3], and Hoffmann electrolysis apparatus^[4]. The current passing through the system as a function of time was collected and analysed by Datastudio software and a graph representing the electrical charge (Q) was produced. The parameters such as, the pressure of water vapour ($P_{w.v.}$), the differential pressure (Δgh), the total pressure (P), the pressure due to hydrogen gas (P_{H_2}) and the constant of Boltzmann constant (k) were calculated using excel spreadsheet.

This designed physical chemistry experiment was enabling instructors and students to perform hands-on experiments based on computer data acquisition system, in which they use the obtained electrical charge to calculate the Boltzmann constant, and to compare the experimental results to the accepted value.

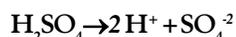
The experimental arrangement was easy to set up and was relatively less time consuming compared to other water electrolysis traditional experiments. Sufficient information and details about the experiment was provided to allow instructors to introduce it into college or undergraduate laboratory course for the determination of the Boltzmann constant, the Avogadro number and the fundamental electronic charge.

Theory

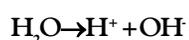
Boltzmann constant can be determined in several ways. This computer-based laboratory was using Hoffman electrolysis apparatus, a power supply, Science Workshop 750 interface, a current sensor and Datastudio software.

Pure water is however a very poor conductor of electricity and one has to add dilute sulphuric acid H_2SO_4 in order to have a significant current flow. The electrodes consist of platinum foil. The aqueous solution of sulphuric acid involves the preparation of hydrogen at the cathode, and the preparation of oxygen at the anode. These gases present a ratio 2 to 1.

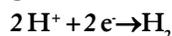
Sulphuric acid is a strong electrolyte is fully dissociated in aqueous solution.



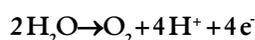
Water is a weak electrolyte and is only slightly dissociated



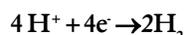
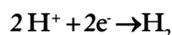
During electrolysis, the hydrogen ions migrates towards the cathode, and are discharged there (i.e. they gain an electron and are converted to hydrogen gas).



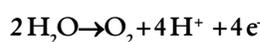
At the anode the concentration of hydroxyl ions is too low to maintain a reaction and the sulphate ions are not oxidized but remain on in solution at the end. Water molecules must be the species reacting at the anode.



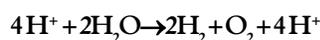
a) Negative electrode (cathode).



b) Positive electrode (anode).



Overall reaction.



For every hydrogen ion discharged at the anode, another hydrogen ion is formed at the cathode. The net result is that the concentration of the sulphuric acid remains constant and this electrolysis consists of the decomposition of water with the overall reaction.



The produced hydrogen and oxygen are both considered as ideal gases. The relation $PV = nRT$ could be applied for one or the other of the gases. As hydrogen is concerned, in the gaseous phase, two gases coexist: hydrogen H_2 and water vapour H_2O .

The partial pressure of a pure body is linked only with its temperature, if it is in equilibrium with the liquid phase. Generally, a good approximation is obtained by using the partial pressure equation, named Antoine's equation^[5,6].

$$\log_{10}(p) = A - B/(t + c)$$

Where is p in mm Hg, t in °C, and A, B and C as a function of each particular body.

For water pressure in the temperature between 0°C and 60°C, the A, B and C parameters are: 8.10765, 1750.286 and 235.0, respectively. To obtain the vapour pressure of water in Pascal (Pa), a conversion from mmHg to Pascal was performed. A factor of conversion is: 1 mm Hg = 1.33322×10^2 Pa. The Antoine's equation in Pascal is written as.

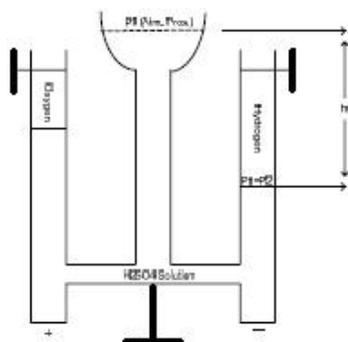


Figure 1 : Differential pressure separated by h between two level liquids of Hoffman electrolysis apparatus

$$\log P^{\circ}H_2O = 10.23 - \frac{1750.28}{T + 235} \quad (1)$$

The total pressure above the solution is the sum of partial pressures

$$P_t = P_{H_2} + P^{\circ}H_2O \quad (2)$$

The differential pressure separated by a height (h), figure 1, between two level liquids is given by.

$$P_2 = P_t = P_1 + \rho_{\text{liquid}} gh \quad (3)$$

ρ_{liquid} is the volume density of the liquid. The density was assumed to be the same as the pure water, 1000 Kg m^{-3} .

g represents the acceleration of gravity = 9.81 m.s^{-2} .

Substituting equations (1) and (3) in equation (2) we obtain the equation describing the hydrogen pressure (P_{H_2}).

$$P_{H_2} = P_t - P^{\circ}H_2O \quad (4)$$

The total charge is the amount of electric current that passes through the low concentration of dissolved H_2SO_4 in a known time interval. The electrolysis process yields hydrogen and oxygen gases. This charge was determined by Datastudio software and is represented by the area under the curve of current versus time. The mathematical form of the electrical charge due to electrolysis is.

$$\text{Charge} = \int_0^t I \cdot dt \quad (4)$$

From the equations described previously, we could derive an expression for k . The Boltzmann constant is defined as a bridge between macroscopic and microscopic physics. Macroscopically, one can

define a (gas scale) absolute temperature as changing in proportion to the product of the pressure P and volume V that a sample of an ideal gas would occupy at the temperature.

$$PV \propto T \quad (6)$$

Introducing Boltzmann constant transforms this into an equation about the microscopic properties of molecules,

$$PV = N \cdot k \cdot T \quad (7)$$

Where N is the number of molecules of gas, k is Boltzmann constant. This reveals kT as a characteristic quantity of the microscopic physics, having the dimensions of energy, and signifying the volume \times pressure per molecule.

$$k = \frac{PV}{NT} \quad (8)$$

Equation (8) may be written as

$$k = \frac{2P_{H_2} V_e}{QT} \quad (9)$$

Where k is Boltzmann constant, 2 represents the number of gram moles in H_2 , e is the electron charge ($= 1.6 \times 10^{-19} \text{ C}$), P_{H_2} pressure due to hydrogen gas, in Pa and V is the volume of H_2 in m^3 , Q is the total charge in C and T represents the temperature in Kelvin.

EXPERIMENTAL

Boltzmann's constant was estimated by means of water electrolysis process. The equipments and apparatus which were used in this work were a computer, Datastudio software for data acquisition, current sensor, Science Workshop 750 interface of PASCO, a 24 V power supply and a Hoffmann electrolysis apparatus as shown in figure 2.

The Hoffmann electrolysis apparatus consists of two vertical 50mL, gas-collecting, graduated glass tubes with stopcocks at top and joined by a bridging tube to a reservoir and fitted with a pair of platinum electrodes at the lower ends of the glass tubes.

A lead wire connecting the platinum electrode passes through the glass tube for external connections, so that only the platinum electrode comes in contact with the electrolyte. Pure water is however

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Figure 2: Experimental setup of the electrolysis apparatus

a very poor conductor of electricity and a water-soluble electrolyte must be added to the electrolysis cell to close the circuit. The electrolyte dissolves and disassociates into cations and anions that carry the current. Electrolytes are normally acids, bases, or salts. The water electrolysis apparatus was filled with 200 ml of aqueous solution of 0.15M H_2SO_4 , in which the gases evolved at the anode and cathode, can be collected in separate graduated tubes. When the solution is electrolysed, hydrogen is produced at the cathode and oxygen at the anode. The ratio by volume, of hydrogen to oxygen is 2 to 1.

A power source delivering 24V was connected to the electrodes of Hoffmann's electrolysis apparatus via a current sensor. The current applied for water electrolysis was monitored by the current sensor and controlled by Datastudio Software of PASCO, and its mean value was varying from 81 to 82 mA for different trials. The sensor was linked to a computer through a Science Workshop 750 interface of PASCO.

The value of electrical charge Q was calculated by the software in real-time from the data acquisition of current as a function of time. A plot showing the area which represents the integral of current as a

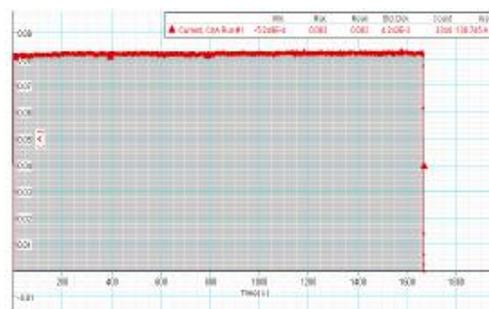


Figure 3 : Graph of electrical charge of water electrolysis hydrogen volume = 17ml, electric charge = 136.745 C

function of time from t_1 = the beginning of the electrolysis and t_2 = the end of the electrolysis, was displayed on the computer. A typical graph of electrical charge for hydrogen gas volume of 17ml was given in figure 3.

The height differential was measured accurately for each trial. Room temperature and atmospheric pressure were registered for each experiment.

In all five trials of the experiment were carried out in the laboratory, where the first two trials were achieved in one day and the other three were carried out another day. The collected hydrogen volumes were from 13 to 17ml. These volumes were used for calculating the average value of Boltzmann constant.

RESULTS AND DISCUSSION

The experimental data for the five trials were calculated with excel spreadsheet, and were presented in TABLE 1. The pressure of water vapour P_{H_2O} was calculated using Antoine's equation, equation (1) and the pressure due to hydrogen gas was obtained by means of equation(4). The values of Boltzmann

TABLE 1 : Typical data and their analysis with excel spreadsheet

H_2 (m ³)	h (m)	T (°C)	P_{atm} (Pa)	Charge (C)	$P_{v,w}$ (Pa)	ρ_{gh} (Pa)	P_{tot} (Pa)	P_{H_2} (Pa)	K (J/K)
1,30E-05	1,42E-01	22	101100	102,47	2 634,28	1393,02	102493,02	99858,74	1,37E-23
1,40E-05	1,48E-01	22	101100	110,23	2 634,28	1451,88	102551,88	99917,60	1,37E-23
1,50E-05	1,58E-01	23	103300	120,76	2 799,33	1549,98	104849,98	102050,65	1,37E-23
1,60E-05	1,67E-01	23	103300	128,90	2 799,33	1638,27	104938,27	102138,94	1,37E-23
1,70E-05	1,72E-01	23	103300	136,75	2 799,33	1687,32	104987,32	102187,99	1,37E-23
Average =									1,376E-23
STDEV =									0.001E-23

Estimated Error % \approx 0,3

constant were estimated using equation(9). The data were collected for 20 to 30minutes, an interval sufficient to produce significant hydrogen volume between 13 to 20 ml. A typical graph of current passing through the circuit system versus time was shown in figure 3, in which the electrical charge Q and the average applied current I were given in the plot.

To illustrate the way how Boltzmann constant value was obtained by calculation, the measurements of trial 5 were given as an example.

- Pressure due to water vapour, equation (1)

$$\text{Log}P^{\circ}_{\text{H}_2\text{O}} = 10.23 - \frac{1750}{23 + 235} \quad (1)$$

$$P^{\circ}_{\text{H}_2\text{O}} = 2799,33\text{Pa}$$

- Differential pressure between the two liquids (2)

$$\rho_{\text{liquid}} gh = 1000 \times 9.81 \times 0.172 \quad (2)$$

$$= 1687,32\text{ Pa}$$

- Total pressure, equation (3)

$$P_t = P_1 \rho_{\text{liquid}} gh \quad (3)$$

$$P_t = 103300 + 1687,32\text{ Pa}$$

$$= 104987,32\text{ Pa}$$

- Pressure due to hydrogen gas, equation (4)

$$P_{\text{H}_2} = P_t - P^{\circ}_{\text{H}_2\text{O}} \quad (4)$$

$$= 104987.32 - 2799.33$$

$$= 102187,99\text{ Pa}$$

- Boltzmann's constant, equation (9)

$$k = \frac{2P_{\text{H}_2} V e}{QT} \quad (9)$$

$$= \frac{2 \times 102187,99 \times 17 \times 10^{-6} \times 1,6 \times 10^{-19}}{136745 \times 296}$$

$$= 1,378 \times 10^{-23} \text{JK}^{-1}$$

The pressure of water vapour $P_{w,v}$, the relative pressure Vgh , the total pressure P_{tot} and the pressure of hydrogen gas were given in columns 6, 7, 8 and 9, respectively. The values of Boltzmann constant were given in the last column.

Error analysis

The estimated uncertainties in the measured values are. $\Delta Q = 0.2\text{ AS}$, $\Delta T = \pm 0.2\text{ K}$, $\Delta V = \pm 0.1 \times 10^{-6}\text{ m}^3$, $\Delta P_{\text{H}_2} = \pm 95\text{ Pa}$.

The Boltzman constant, $k = 1.378 \times 10^{-23} \text{JK}^{-1}$,

where the relative uncertainty in k was obtained by adding the fractional uncertainties in quadrature.

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\Delta P_{\text{H}_2}}{P_{\text{H}_2}}\right)^2 + \left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta Q}{Q}\right)^2 + \left(\frac{\Delta T}{T}\right)^2$$

$$\left(\frac{\Delta k}{k}\right) = 0.0061$$

$$\Delta k = 8.4 \times 10^{-26} \text{JK}^{-1}$$

The yielded experimental result was $1.378 \times 10^{-23} \text{JK}^{-1}$ with an uncertainty of $\Delta k = 8.4 \times 10^{-26} \text{JK}^{-1}$.

To investigate the error on the reproducibility of the repeated experiment, the standard deviation for five samples was estimated as follows.

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$

Where: X_i : i^{th} value, obtained from a series of measurements for one sample,

\bar{X} : mean value of n measurements,

n : Number of measurements.

The average value of Boltzmann constant, $k = 1.376 \times 10^{-23} \text{JK}^{-1}$ with a standard deviation $\sigma = \pm 0.001 \times 10^{-23}$. The average experimental result matches quite well with the theoretical value of Boltzmann constant. The relative error between accepted and repeated experimental value of k was approximately 0.3%.

Hazards

Concentrated sulphuric acid H_2SO_4 is highly corrosive to all parts of the body and is considered not to be a developmental toxicant. When handling the acid, care must be taken to avoid spills over the solution, wear eye and hand protection and provide adequate ventilation. When diluting, always add acid to water, not water to the acid. There are no other unusual hazards in this experiment, apart from the dilution of the concentrated sulphuric acid.

CONCLUSION

The experiment provides teachers and students with sufficient details to estimate Boltzmann constant, using a computer-based laboratory with a

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Hoffman electrolysis apparatus. The use of the computer based data acquisition system improves the accuracy and the precision of data measurements of the electrical charge.

Students performing this practical work indicated that the computerised laboratory enhanced their learning experience and helped increase their knowledge of the importance role computers can play in data acquisition and analysis.

In terms of comparative results, the average experimental value was approximately the same as the accepted Boltzmann constant, with a percentage error of approximately 0.3 %. The value of Boltzmann constant obtained by the use of computer-based laboratory method was more precise than other methods found in literature [7] and [2], were the percentage errors were approximately 2 % and 9 % for the determination of k from the root-mean-square displacement and via probability distribution and around 3 % for the calculation of k from the fundamental charge via the electrolysis of water, respectively.

This experiment is also a good application for the determination of Avogadro's number, the determination of the fundamental electronic charge and understanding the principal of ideal gas law.

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