Equilibrium Constant and Temperature of the solution

Introduction

pH is a measure of the acidity or alkalinity of a solution. Solutions with a pH less than seven are considered acidic, while those with a pH greater than seven are considered basic (alkaline). An acid dissociation constant, denoted by K_a , is the equilibrium constant for the dissociation of a weak acid. According to the Bronsted-Lowry theory of acids and bases an acid is only recognized by its reaction with a base. In aqueous solution the base is water itself.

For most acids, including water, as the temperature increases there will be a decrease in pH. As the solution heats up there will be more chance of the acid molecules ionizing and this will increase the dissociation in the solution. An increased dissociation means a decreased equilibrium constant.

Ka varies with change in temperature according to the Van't Hoff equation. The Van't Hoff equation in chemical thermodynamics relates the change in temperature to the change in the equilibrium constant given the enthalpy change. The equation was first derived by Jacobus Henricus Van't Hoff.

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2}$$
 (Equation 1)

Where K is the equilibrium constant

T is the temperature in Kelvin

H is the enthalpy change

R is the Gas Constant

If we use the relation between Gibbs energy and the equilibrium constant we can rewrite the equation as

$$\ln{(K)} = -\frac{\Delta H^{\circ}}{R} \left[\frac{1}{T}\right] + \frac{\Delta S^{\circ}}{R} \tag{Equation 2}$$

Where S is the change in Entropy and rests all is the same as the above equation 1. According to the equation 2 there will be an inverse relation between ln Ka and Temperature. Since Ka is less than 1, this means that as temperature increases, Ka increases. (www.ualberta.ca/~jplambec/che/p102/p02062)

Design

Research Question

What is the relationship between the equilibrium constant of acetic acid and the temperature?

Variables

Independent variable: The temperature of the acid

Dependent variable: The equilibrium constant of the acid

Controlled variables: The concentration of solution. Same pH meter was used. Same amount of acid was used for each trial.

Materials Required

- Laptop
- Logger Pro
- ✤ Heater
- ✤ 0.1 M Acetic acid
- ✤ Thermometer

Procedure

First a beaker was filled with 50 ml of acetic acid using a 50 ml of pipette. Then the ph meter was calibrated using the buffer of pH 4 and pH 7. After calibrating the pH meter the uncertainty in the pH was determined by reading the pH of the buffer solutions. Then the acid in the beaker was cooled to 10°C using a beaker which had ice and water in it. After the acid reached the temperature of 10°C, the pH of the acid was measured for 10 seconds and then the average of the pH was taken. The average was recorded as the pH of the acid at 10°C. The same technique was used to measure the pH for 6 different temperatures ranging

- Beaker
- Buffer of pH 4 and pH 7
- ✤ pH meter
- ✤ distilled water
- ✤ Pipette of 50 ml



Figure 1: Set up of Experiment the pH meter was connected to the computer via logger pro. This is not show in the picture.

from 10°C to 70°C. After taking the pH at all those temperature the whole procedure was repeated twice more so that we can have three different trials. For the set up of the experiment see figure 1.

Data Collection and Processing

Temperature(±0.1°C)	pH (±0.1)			
	Trial 1	Trial 2	Trial 3	Average
10.0	3.2	3.3	3.1	3.2
20.0	3.0	3.0	3.0	3.0
30.0	2.9	2.9	2.8	2.9
40.0	2.7	2.7	2.7	2.7
50.0	2.6	2.6	2.5	2.6
60.0	2.4	2.4	2.4	2.4
70.0	2.3	2.3	2.3	2.3

Table 1: Temperature and pH data.

Table 1: This table shows the pH at different temperatures of acetic acid for all the trials and the average of the all the pH. Uncertainties in temperature were calculated by measuring the change in the temperature while measuring the pH. Uncertainties in pH were measured by checking the difference in actual pH and the pH measured by the pH meter.

Sample Calculations

First the average of the pH from the three trials were taken and then the value of equilibrium constant (Ka) was calculated.

Calculation of Ka

First the concentration of H⁺ was calculated.

 $[H^+] = 10^{-pH}$, Therefore for first trial, $[H^+] = 10^{-3.2} = 6.30957 * 10^{-4}$

Same way [H⁺] was calculated for other temperatures as well.

As this is a weak acid concentration of acetate ion is also equal to the [H⁺]

Therefore, $Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

For the first temperature of 10° C Ka = $3.98107 * 10^{-6}$

Same way Calculation was done for other temperatures.

Calculation of Uncertainty in Ka

First the value of Ka was calculated.

For example: Ka value for the temperature 10° C is 3.98×10^{-6} at 3.2 pH

Then the value of Ka with pH of 3.1 was calculated as uncertainty in pH is 0.1

So Ka at 3.1 is 6.31 * 10⁻⁶.

Now the value of Ka for 3.2 pH was divided by the value of 3.1 pH and then it was multiplied by 100 to calculate the percentage.

So, uncertainty = $\frac{3.98 \times 10^{-6}}{6.31 \times 10^{-6}} \times 100 = 63\%$, so uncertainty is 37%

Table 2: Temperature vs. Ka.

Temperature(±0.1°C)	Equilibrium Constant (Ka) (±37%)		
10.0	$3.98 * 10^{-6}$		
20.0	8.71 * 10 ⁻⁶		
30.0	$1.82 * 10^{-5}$		
40.0	$4.37 * 10^{-5}$		
50.0	7.94 * 10 ⁻⁵		
60.0	$1.51 * 10^{-4}$		
70.0	$2.51 * 10^{-4}$		

Table 2: This table shows the value of Ka at different temperatures of acetic acid.



Graph 1: This is the graph between dissociation constant and Temperature. This graph has got a power fit. This graph shows that the value of Ka does not increase linearly with temperature.



Graph 2: This Graph is between natural log of Ka and inverse of temperature. This graph shows that the natural log of Ka is inversely proportional to temperature of the solution in Kelvin. According to theory, the slope of this is equal to the change in enthalpy divided by Gas constant. The y- intercept is the value of change in Entropy divided by the Gas Constant.

Conclusion

The results from graph2 clearly support the hypothesis. According to graph2 the Ka increases as there is increase in the temperature and it also shows that the ln Ka is inversely proportional to Temperature. The Equation which we get from graph 2 is:

$$ln Ka = \frac{(-6.0 \times 10^{2} \pm 1.1 \times 10^{2})}{T(K)} + (12.00 \pm 0.36)$$
(Equation 3)

The Slope in this equation is expected to be the value of -H/R where H is the change in enthalpy and R is the Gas constant.

The Y-intercept in this equation is expected to be the value of S/R where S is the change in entropy.

This experiment was done within a temperature range of 10°C to 70°C so validity of the equation above is reliable within this range. Beyond this temperature range, it is unknown if the equation remains valid as it was not tested.

The Van't Hoff equation was strongly supported as graph 2 was clearly showed the inverse relationship and linear fit was within the uncertainty range for all points.

Evaluation

Even though the experiment was conducted very carefully to minimize the errors, but still we had some errors which might have change the results.

The main weakness of this investigation was the extreme unreliability of the pH meters. The readings changed over time and oscillated during each trial. An uncertainty of 0.1 in pH represents a 10% uncertainty in the concentration of hydronium ions. A better quality pH meter would increase the reliability of the results significantly.

There could have been an error in the temperature reading during the pH reading. The temperature might have changed within 10 seconds. This could have caused some of error in the reading of the ph and as a result could have affected the value of Ka. The pH should have been taken when the temperature would have stabilized.

Another error was the stirring of the solution. The pH meter was used to stir the solution. Stirring with the pH meter may have resulted in bouncing in pH readings which may have affected the final graph. In order to improve this error a proper stirring device must have been used so that the pH meter could remain still during readings.