

8.02 ENTHALPIES AND ENTROPIES OF REACTION BY SOLUTION CALORIMETRY

(4 points)

To find the enthalpy change that accompanies a reaction, we could measure the temperature rise or fall when a known amount of reaction takes place in a thermally isolated system, such as a calorimeter. We need to know the heat capacity of the calorimeter and its contents, and also how much heat is transferred to or from the surroundings, (or alternatively, be able to minimize that heat transfer).

In this experiment, reactant solutions are mixed in a Dewar flask, which forms an effective calorimeter. The heat capacity of the Dewar and contents is determined by passing a known amount of electricity through the system, after the reaction is complete, and determining the resulting temperature change. The temperature rise on reaction is small, ($<1\text{K}$) and could be measured using a precision thermometer such as a Beckmann, but this type of thermometer has a large heat capacity, so a thermistor is used instead.

In the experiment you will measure the enthalpies of formation of two complexes. Using the relevant equilibrium constants, the free energies of reaction can be calculated, and from the measured enthalpies, the entropy change accompanying the reaction can be found.

Background information

This experiment makes use of simple thermodynamics arguments; you do not need any 2nd year level courses to be able to understand and carry out the experiment.

Relevant lecture course: Introduction to thermodynamics (1st year).

Experiment URL:

<http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/802.html>

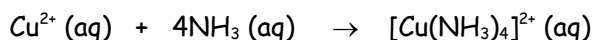
Safety/COSHH

The vapours of 1,2-diaminoethane and ammonia are harmful and are irritating to the skin, eyes and respiratory system. Both chemicals are very damaging if splashed in the eyes; it is essential that you wear safety glasses. Use the fume cupboard whenever possible. In a small proportion of people, 1,2-diaminoethane acts as a sensitizer; take care to ensure that the solution does not come into contact with your skin. Disposable gloves are available. There is further information in Appendix A about the chemicals used in this experiments.

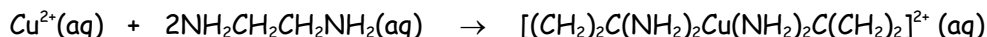
Theory

Stability constant for complex formation

Cu^{2+} ions react with aqueous ammonia to form the cuprammonium complex:



Cu^{2+} also reacts with 1,2-diaminoethane (ethylenediamine) to form a chelate compound:



The resulting complex is usually written in the shorthand form $[\text{Cuen}_2]$. The ammonia and 1,2-diaminoethane in the reactions shown above are acting as ligands, as they are donor partners in coordinate bonds. If we denote metal ions as M and ligands as L, the reactions may be written:



The corresponding equilibrium constant in terms of activities is

$$K = \frac{a_{\text{ML}_v}}{a_{\text{M}}a_{\text{L}}^v} \quad (2)$$

This is the limiting value at infinite dilution of K_c , the equilibrium constant (stability constant) in terms of concentrations, since, as the concentration becomes very small, the activity coefficient approaches unity.

Measurement of enthalpy of reaction

When either of the reactions shown above occurs, heat is almost sure to be released or absorbed, since few reactions are thermally neutral. Let the temperature change on the formation of n moles of complex be ΔT_r . Since the reactions occur at constant pressure, it is the enthalpy of formation of a mole of complex, $-\Delta H$, which is measured, and

$$-\Delta H = [\Delta T_r C_p] / n \quad (3)$$

where C_p is the heat capacity of the calorimeter and its contents.

In order to determine how much heat is released, we need to find the temperature rise when a defined amount of energy is put in. This is done, in this experiment, by heating the solution electrically.

Suppose that, instead of the reaction occurring, a current i at voltage V is switched through the heater for time t , and that the temperature then rises by an amount ΔT_h . The energy E put into the system by the heater is

$$E = V i t = \Delta T_h C_p \quad (4)$$

In practice, V and i vary slightly with time, but the variation is not sufficient to concern us in this experiment. Eliminating C_p from equations 3 and 4:

$$-\Delta H = [\Delta T_r V i t] / [\Delta T_h n] \quad (5)$$

If a thermistor of resistance R is used to measure the temperature changes, then, since ΔT is approximately equal to $-\Delta \log R$ (which is not equal to $-\log \Delta R$!), equation 5 becomes

$$-\Delta H = [(\Delta \log R)_r V i t] / [n (\Delta \log R)_h] \quad (6)$$

Thermodynamic equations

A reminder from first year thermodynamics: consideration of the chemical potentials of reactants and products in an equilibrium reaction leads to the Van't Hoff isotherm:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

where ΔG° is the standard free energy change of a mole of reaction. Thus, if the value of K is known, ΔG° may be calculated. If ΔH has been measured, and it is assumed that $\Delta H = \Delta H^\circ$, ΔS° may be found from the definition of G

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

Procedure

The apparatus is sketched in Fig. 1. Through the lid of a Dewar flask is mounted a thermistor (whose resistance changes as a function of temperature) in a protective steel tube. The thermistor is immersed in a high-boiling liquid (dibutyl phthalate) to enhance thermal contact with its surroundings. A stirrer, heater and a siphon also pass through the lid. Current for the heater is supplied from an adjustable, stabilized power supply. A change-over switch connects this with the calorimeter, or with a dummy heater of the same resistance. The use of the dummy heater allows the current to be adjusted and to settle before the calorimeter itself is heated. The calorimeter heater should never be switched on in air, or it will burn out. A thermistor is used for temperature measurement, and its resistance is determined with a multimeter.

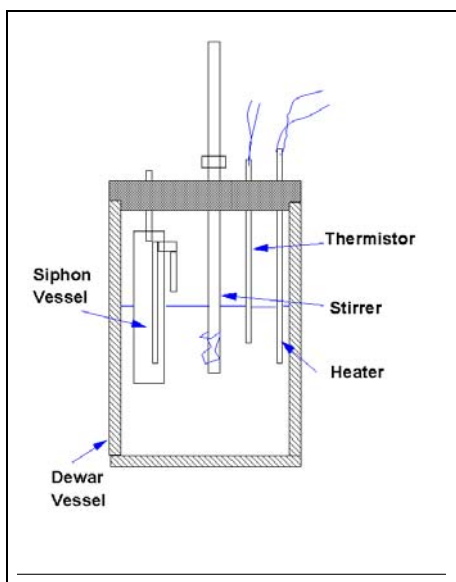


Fig. 1. The calorimeter used in the experiment.

Preparation of reactant solutions

Make up accurately 250 cm³ of 0.2M copper sulfate solution, using CuSO₄·5H₂O and deionized water. Check that the concentration of the ammonium hydroxide solution supplied is between 3M and 5M by titrating it against a standardized strong acid, with methyl red as indicator. A 2M solution of 1,2-diaminoethane is supplied.

Setting up the calorimeter

Wash out the Dewar with deionized water. If the glass siphon is attached to the lid, remove it carefully, holding it near the top of the vertical stem and twisting gently to remove it from the pipette filler. Wash the siphon with deionized water. Wash the stirrer, heater coil and thermistor by raising a beaker of deionized water up to the lid. Remove excess water from the siphon, but do not bother to try to dry the inside, since traces of water in siphon or calorimeter will not affect the results.

Rest the siphon in a 250 cm³ beaker and place it in a fume cupboard. Using a 5 or 10 cm³ syringe from the service room, add 15 cm³ of the ammonia solution to the siphon. This reactant will be in excess. Pipette 50 cm³ of the copper solution (do not pipette by mouth as copper solutions are poisonous) into the Dewar flask. Measure 250cm³ deionized water into a measuring cylinder and adjust its

temperature to 23-27°C by running hot or cold water over the outside of the cylinder. Add to the contents of the Dewar.

Return the siphon to its position in the lid, holding it in place by connecting the pipette filler above the lid. Check that the stirrer will not foul the siphon when the motor is running. Carefully position the Dewar under the lid, then slide the labjack under the Dewar and raise the Dewar so that it is just touching the lid, but is not tight against it. Turn the stirrer controller on and adjust the stirring rate to 5 Hz.

Connect the power supply and dummy heater. Connect the thermistor to the multimeter. Check that the change-over switch is connected to the dummy heater, then switch on the current and thermistor circuit. Leave both running throughout the experiment. Adjust the current to give a current near 400 mA.

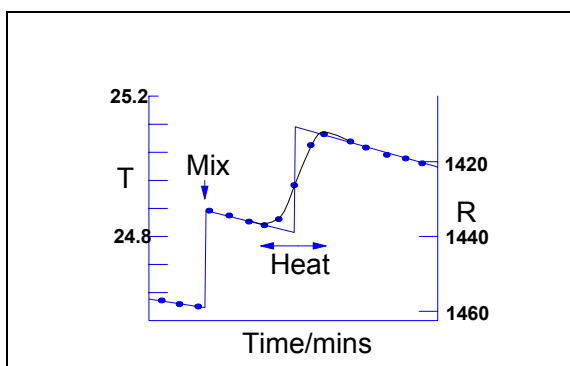


Fig. 2. The variation of temperature and resistance in the calorimeter with time.

Temperature measurement

First observe any temperature change in the calorimeter due to heat transfer with the environment. Record and plot the resistance of the thermistor for five one-minute intervals. If, after this time, the drift in the resistance is greater than $2.5 \Omega \text{ min}^{-1}$, continue the observations until the drift lies within this range.

Press the bulb attached to the siphon to send over the ammonium hydroxide into the copper solution to form the chelate. Stop when all the ammonia solution has been pushed over (which can be confirmed by looking through the Pyrex top, or by the sound of air blowing through the siphon). Record and plot the resistance at one-minute intervals until the resistance settles, showing that thermal equilibrium has been reached.

Now carry out the calibration. At the same moment as starting a timer, operate the change-over switch to turn on the heater. Continue recording the resistance at one-minute intervals. Half way during your measurements, note the voltage and current being passed through the heater. After exactly ten minutes, turn off the heater. Continue to record the resistance until the readings stabilize.

Repeat the experiment with 2M 1,2-diaminoethane in place of the ammonia solution. Then carry out one of the determinations a second time to check consistency.

At the end of the experiment switch off and disconnect all electrical circuits. Wash out the calorimeter and associated apparatus with deionized water.

Calculations

Calculate the concentration of the ammonium hydroxide solution. Draw graphs of decreasing $\log R$ (increasing T), against time for each run. Calculate the values of $(\Delta \log R)_r$ and $(\Delta \log R)_h$. Find the enthalpies of formation of the cuprammonium and $[\text{Cu en}_2]^{2+}$ complexes at the temperature of the experiment. You may assume this enthalpy equals the standard enthalpy of formation at 25°C .

Comment on the consistency of the duplicate experiments that you have performed, explaining in detail any differences.

The stability constants of the cuprammonium and $[\text{Cu en}_2]$ complexes at 298K, in solutions of similar ionic strength to those used in the experiment, are given by $\log_{10} K = 13.0$ and 20.0 respectively [4]. Use these data to calculate the free energies of the reactions and so find the entropy of formation for the complexes.

References

1. *Textbook of Pharmacology*, W.C.Bowman and M.J.Rand, Blackwell, Oxford, 2nd ed. (1980) [Hooke Re9]
2. Linearized Thermistor Bridge for Calorimetry, S.R.Gunn, *J. Chem.Educ.*, **50**, 515 (1973).
3. A solution Calorimeter and Thermistor Bridge for Undergraduate Laboratories, R.A.Bailey and J.W.Zubrick, *J. Chem. Educ.*, **58**, 732, (1981)
4. Stability Constants of Metal-Ion Complexes, L.G.Sillen, *Chemical Society Special Publications Nos 17 and 25*, Chemical Society, London (1964 and 1971).
5. *Advanced Inorganic Chemistry*, F.A.Cotton and G.Wilkinson, 6th edn, Wiley Interscience, New York (1999). [Hooke C61]

Appendix A. Chemical Properties, Hazards and Emergency Treatment

Wear gloves for any operations in which you will be handling ammonia or the amine. Neoprene and nitrile are both suitable materials.

Ammonium hydroxide solution

Colourless liquid. Ammonia solution is corrosive and can cause burns at moderate concentration. The principle danger is to the eyes - alkali at a concentration of 5M, as used in this experiment, can cause serious burns to the eyes, so safety glasses are essential. If ammonia solution is splashed into the eyes, immediately call for assistance and wash the eyes thoroughly with water. For further information, see:

http://ptcl.chem.ox.ac.uk/MSDS/AM/ammonium_hydroxide.html

Copper sulfate

Blue crystalline solid. Copper sulfate is harmful if you swallow or inhaled it, so be carefully not to breathe in any dust while preparing the solutions. For further information, see:

http://ptcl.chem.ox.ac.uk/CO/copper_II_sulfate.html

1,2-diaminoethane

Supplied as a colourless solution (2M). This presents hazards similar to those of ammonium hydroxide solution. Keep it off your skin and well away from the eyes. In sensitive people it may produce an allergic reaction, so if you get it on the skin, wash it off immediately. If you feel unwell or develop a skin rash or itchiness, contact a demonstrator or first aider immediately. For further information, see:

<http://ptcl.chem.ox.ac.uk/MSDS/ET/ethylenediamine.html>

Appendix B. Problems and Solutions

Observation	Indicates	Solution
DVM reading does not change	a) DVM is set up to record something other than resistance b) Solutions are of the wrong concentration c) Solution has not been blown out from the sample holder d) Thermocouple is not immersed in liquid e) Heater has been switched on in air and has burnt out	a) Ensure that the dial on the DVM is turned to Ω b) Check concentrations c) Check the connection between pipette filler and siphon; unless no solution has been blown out from the siphon, the experiment will have to be restarted d) Withdraw the Dewar and check the positioning of the thermocouple e) Bad news! See the technician and ask for the heater to be repaired; experiment will have to be halted for the session
DVM shows no reading	DVM battery dead	Ask technician to replace battery
Resistance shown on the DVM changes constantly	Heater in solution is turned on	Check that the heater has not been inadvertently switched on; heater should only be used after the reaction is complete