solutes of high molecular weight, and for solvents of low molecular weight. When the solubility is expressed as amount of solute in a given volume of the solvent, it is greatest for solvents having low molecular weight and high density.

(2) Deviations from Raoult's law may be ascribed primarily to inequality of internal pressure and to polarity. These factors, and their approximate prediction, have been discussed at some length for various kinds of liquids.

(*a*) Nonpolar liquids having approximately equal internal pressures obey Raoult's law, and are subject to the previous generalizations.

(*b*) A difference in internal pressure, with nonpolar liquids, produces a positive deviation from Raoult's law for both components, decreasing the solubility, whether considered with respect to a gaseous or a solid form of the component in question. Very great differences in internal pressure are necessary for incomplete miscibility of the two components in the liquid form.

(*c*) A polar and a nonpolar liquid show strong positive deviations from Raoult's law, with accompanying effects on solubilities. Most liquids which are not completely miscible belong to this class.

(*d*) Two polar liquids may show either positive or negative deviations from Raoult's law, usually positive where there is considerable difference in polarity, and negative when both are highly polar. The effects on solubility correspond to the direction of these deviations.

Numerous examples are given justifying the points of view presented.

BERKELEY. CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.]

AN ADIABATIC CALORIMETER.

BY FARRINGTON DANIELS.

Received May 2, 1916.

The cooling correction, which is essential in ordinary calorimetry, is troublesome and uncertain. The adiabatic calorimeter as devised by Richards eliminates this correction, but since it has not received the general acceptance which, in the opinion of the author, it deserves,[1] an attempt has been made in this laboratory to modify the construction so as to bring it into more popular favor. Electrolytic heating, as used by Derby, has made possible the development of a calorimeter which it is hoped will accomplish this purpose.

In common calorimetric practice the temperature is read at frequent intervals and the correction for radiation is calculated by one of several

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[1] See criticisms of Dickinson, Bureau of Standards, *Bull.* 11, 206 (1914), and of Jaeger and von Steinwehr, *Z. physik. Chem.*, 54, 428 (1906).

formulae, the best of which is that of Regnault-Pfaunder.[1] Even this is open to objection except for small temperature changes. For commercial work its use entails too much labor, and simpler but less accurate approximations are employed. The simplest method of eliminating radiation is that which employs a vacuum jacketed calorimeter. This is wholly satisfactory in many cases but conduction through the glass may introduce a large and ill-defined heat capacity and if the temperature is not close to that of the room, appreciable exchange of heat with the environment does take place. Furthermore, at high temperatures, condensation of vapor on the cooler cover and upper walls may introduce considerable errors from evaporation.

These difficulties are overcome in the adiabatic calorimeter of Richards, which has been used in the extensive thermo-chemical investigations of high precision at Harvard University.[2] It is so arranged that the temperature of an outer jacket is raised at a rate equal to the rate of rise in the calorimeter. Thus there can be no exchange of heat with the environment. The outer jacket is filled with a strong solution of sodium hydroxide and sulfuric acid is added from a buret as needed, to keep the two temperatures always equal.

The use of strong alkali, however, is objectionable as well as expensive and electrical heating coils may be used instead, as suggested in Richards' first paper. Benedict and Higgins[3] described such a calorimeter in which there was a lag of nearly a minute, necessitating preliminary experiments and giving a determination adiabatic to only about 0.1°. Slevenski and Pakovitch[4] have appreciated the advantages of the adiabatic calorimeter. They filled an outer jacket with kerosene and heated it with coils of iron wire of special design. Their results are satisfactory although they are able to keep the process adiabatic to only 0.1° or 0.2°. In work with Professor Richards, as yet unpublished, the author used a small calorimeter in which a heating coil of nichrome wire was placed in an outer bath of oil. Fifteen seconds were usually required after closing the electrical circuit before the Beckmann thermometer was affected. This time lag was troublesome, but with a slow and regular rise the determination could be kept adiabatic to within 0.02° with the help of a rheostat and a previous calibration.

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[1] *Pogg. Ann.*, **129**, 113 (1866).

[2] *Proc. Am. Acad.*, **41**, 3 (1905); **42**, 573 (1907); **43**, 475 (1908); THIS JOURNAL, **31**, 1275 (1909); **32**, 268, 431, 1176 (1910); **33**, 863 (1911); **37**, 993 (1915); *Proc. Am. Acad.*, **49**, 173 (1913).

[3] THIS JOURNAL, **32**, 461 (1910).

[4] *J. Russ. Phys. Chem. Soc.*, **46**, 1284 (1914). These authors have criticized the descriptions of Richards' calorimeter as being inadequate but the details concerning stirring and adiabatic control for which they searched may be found in the works already cited (THIS JOURNAL, **32**, 447-450 (1910)), for example.

For rapid or irregular rises electric heating with coils is wholly inadequate and it becomes necessary to eliminate the time lag. Dr. Derby has shown how this can be done in electrolytically heated thermostats[1] and the application to adiabatic calorimeters is obvious. By making the whole water jacket itself the conductor, its temperature rises instantly and uniformly throughout with the passage of the current. In this way it is not necessary to wait for a resistance wire to heat up before the temperature of the bath rises, and rapid stirring becomes unimportant for the heat is not localized.

The construction of a calorimeter along these lines is a simple matter. The one which is shown in Fig. 1 has been in successful operation in this laboratory for over a year, and because it embraces some new features, a brief description is offered. The inner can, A, of thin copper, is filled with water (about half a liter). It contains the source of heat, B, which may be, for example, a combustion bomb or an electric heating coil. It is set into a slightly larger vessel, C, and supported on short pieces of very fine glass tubing so that there is everywhere an air gap of half a centimeter between the walls. Three of these glass supports are soldered to the bottom and six to the sides.[2] A brass collar, D, is soldered to the vessel C, and it is tapered so that a brass cover, E, sets down into it snugly as a ground-glass stopper fits into its bottle. This ring and cover are easily turned out by any machinist in a few hours and ground with emery to give a water-tight joint. Various types of screw covers and rubber rings were tried, but none approached this in simplicity of operation and absolute protection from leakage. The inner vessel is plated with silver and the outer one with nickel, except at the ground joint. They

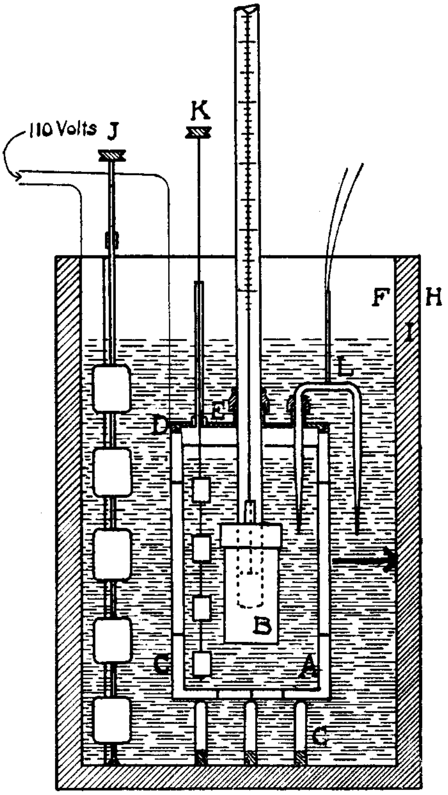

Fig. 1.

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[1] THIS JOURNAL, 35, 1767 (1913).

[2] Glass may be soldered to metal readily if it is first roughened with a file or with hydrofluoric acid, platinized and then copper plated.

are supported in a large copper vessel, F, by nine glass tubes G fitting snugly over short brass rods soldered to it. A still larger vessel H, and a packing, I, of insulating material (kieselguhr) diminish the radiation. A stirrer, J, of the propeller type with four blades bent into the form of a screw is driven by a small water motor. A small, semicircular compartment opens from the vessel F, and the stirrer is so placed that half of its revolution is made in the main part of the jacket and half in the compartment.

This arrangement gives a rapid circulation around the sides of the calorimeter and over and under it. The two vessels C and F are connected with the terminals of a 110-volt, alternating current through a knife switch so that the current may be passed directly through the water of the jacket. The stirrer K in the inner can is similar to J, but much smaller. It revolves in a metal sheath which is insulated from the cover by glass tubing. All tubes leading into the calorimeter, whether of glass or of metal, are soldered to the cover and there is, accordingly, no danger from leakage. In order to cut down the space into which the liquid can vaporize, a thin strip of mica is wired around the top of the can, A, and projects above it so as to touch the cover. With this arrangement, liquid can not evaporate to fill the air space at the sides and bottom, but only at the top.

In most adiabatic calorimetry two thermometers have been used, one in the calorimeter and one in the jacket. Rapid readings entail a considerable strain on the observer, so a thermocouple, L, is substituted for them, thereby simplifying the manipulation and increasing the accuracy.[1] The filament of an ordinary tungsten light or a Nernst lamp is focused through a reading lens to a galvanometer and thence to a ground-glass scale or a white paper scale in a dark box. The thermocouple consists of eight copper-constantan junctions packed in paraffin and enclosed in a tapering sheath of very thin glass.[2] The galvanometer (type P as manufactured by Leeds and Northrup) is placed about five meters from the scale and calorimeter. A difference in temperature of 0.01° between the inner can and the jacket gives then a deflection of about 1 cm. which may be read without difficulty at a considerable distance.

When the outer jacket is too cold the switch is closed, the alternating current passes through the water of the jacket and the temperature rises instantly. When the thermocouple registers zero the switch is opened and the heating ceases almost at once. With a slow rise of 0.2° per minute, or less, it is easy to keep the temperature of the jacket always within 0.01° of the temperature of the calorimeter. With a rapid rise of 1° per minute the process may be kept adiabatic to within 0.02 or 0.03.

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[1] Dickinson has used a thermocouple in an adiabatic calorimeter, Bureau of Standards, *Bull.* **11**, 242 (1914).

[2] See White, THIS JOURNAL, **36**, 2300 (1914) and Adams, *Ibid.*, **37**, 484 (1915).

The following test was made, in which the inner liquid was heated intermittently with an electric heating coil so as to obtain an irregular rise. A boy of high school age, after fifteen minutes' practice, watched the thermocouple scale and controlled the switch, while a second observer recorded the temperature of the calorimeter as registered on a thermometer, and the difference between it and the temperature of the jacket as registered by the thermocouple.

Time.		Temperature calorimeter.	Temperature jacket.
Minutes.	Seconds.		
0	0	28.25	—0.01
0	15	28.60	±0.00
0	30	28.80	—0.02
0	15	28.90	±0.00
1	00	29.20	—0.01
1	15	29.40	—0.03
1	30	29.80	—0.02
1	45	30.20	+0.01
2	00	30.50	+0.03
2	15	30.60	—0.00
2	30	30.80	—0.05
2	45	31.20	—0.01
3	00	31.40	±0.00

The limits of error allowable in the adiabatic control were determined experimentally. It was found that if the temperature of the jacket differed from the temperature of the calorimeter by 0.1° an exchange of heat took place at the rate of 0.5 calorie per minute. If the difference was 0.01°, the heat transfer was 0.05 calorie per minute. This value is of the same order as that found by Richards and Burgess and by Slevenski and Pakovitch in adiabatic calorimeters of larger dimensions. If there is a continuous error of 0.01° in the adiabatic regulation of a calorimeter holding 1 liter an error of 0.01% would be introduced in a determination lasting ten minutes where there was a rise of 5°. Since large errors in the adiabatic control exist but momentarily and since positive and negative differences tend to cancel each other it is safe to say that in the calorimeter described above the AVERAGE difference between jacket and calorimeter may be kept less than 0.01°. This difference could be made smaller by using a more sensitive galvanometer or by increasing the number of junctions in the thermocouple.

With the beam of light from the thermocouple circuit swinging back and forth, the next advance was the automatic control of the heating circuit by means of a selenium cell.[1] The general plan is shown in Fig. 2. When the jacket and the calorimeter are at the same temperature the thermocouple gives a zero reading, and the light rests on the selenium cell, thereby lowering the resistance and closing the relay which breaks the 110-volt heating current. When the calorimeter heats up a little the beam of light moves off from the selenium cell, the relay opens and the heating circuit is closed. The selenium cell is readily made[2] in a few

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[1] The use of a selenium cell in such a connection had been suggested in conversation by Mr. A. T. Larson of Harvard University.

[2] See *Sci. Amer. Supplement*, Jan. 27 (1912).

hours from a strip of mica which is notched and wound with No. 32 copper wire. Two wires are used, one starting from each end, and they are wound on alternate notches. These wires are not in electrical contact except through the very large surface of selenium which fills the spaces between them. The selenium powder is spread on the cell, heated to its melting point and molded into place between the wires with a hot glass rod, cooled, and annealed for eight hours at 215° C. A rather large cell (3 cm. × 20 cm.) and a broad, bright beam of light are desirable. A Nernst lamp with a small convex lens gives an excellent light at a distance of five meters. The selenium cell is placed at the end of a long, black box to cut out the entrance of all light except that from the galvanometer mirror. The current used in this circuit is very small and about ten volts from dry cells or small storage batteries are sufficient. A powerful relay of 150 ohms is essential, and to prevent a slight sticking of the contacts, it is vibrated gently by a rod which projects from the stand which holds the pulley wheels. Since the movement of the armature is small, the 110-volt circuit can not be used with it directly, for sparking is too great. Accordingly a second cheap relay is operated by a dry cell through the first relay and it in turn controls the heavy current. Occasionally with a rapid rise the beam of light swings beyond the selenium cell and on to the wrong side, upsetting the whole adiabatic control. To prevent this a stout wire is fastened to the galvanometer box in such a way that the mirror is arrested when the jacket becomes too hot. The tension on the spring of the relay requires frequent adjustment but for a slow rise the determination may be kept adiabatic to within 0.02° or 0.03° without attention.

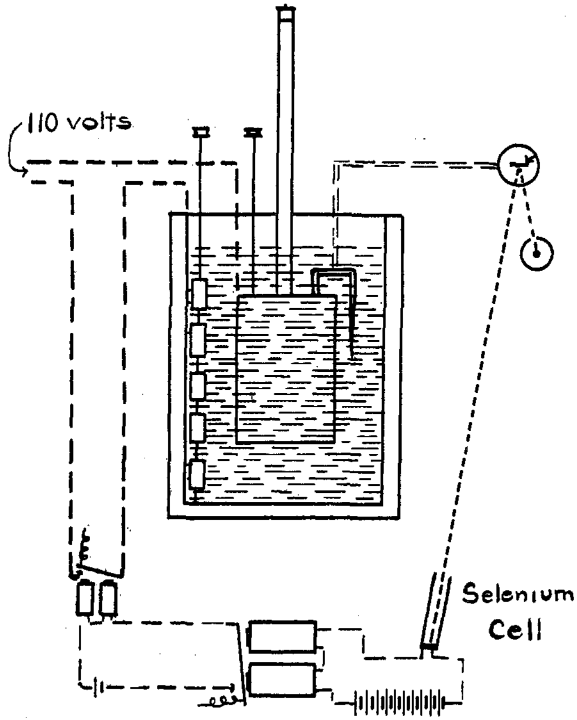

Fig. 2.

This synthermal regulator has advantages over that of Richards and Osgood[1] in that it is small and can be attached readily to any calorimeter without inconvenience. The fact that it requires a galvanometer and a good relay is an objection. Because the regulation by hand is such a simple matter, this selenium cell regulator is not recommended for common calorimetric practice unless a large number of determinations are to be made.

It is by no means difficult to alter an ordinary calorimeter so as to make it adiabatic and in fact some of the well-known calorimeters on the market are already surrounded by water jackets. By cutting the two cans apart, inserting glass supports, and attaching a tight cover, one would have an apparatus similar to the one shown in Fig. 1. Hand stirrers could be used to advantage. Even for very rough work it is worth while to eliminate the cooling correction. The water-tight cover may be omitted and a cheap galvanometer is sufficiently sensitive. The stirrer is unnecessary for the temperature in different parts of the jacket does not vary by more than 0.5°. Experiments with a crude calorimeter constructed in this way showed a cooling effect of 0.08° in ten minutes for a five-degree elevation, whereas under the same conditions without this simple jacket the cooling effect was 0.37°. The rate at which the jacket is heated may be very rapid but then the adiabatic control becomes more difficult. If the current is limited to 6 amperes by a fuse plug, 10,000 calories $\frac{(110 \times 6 \times 60)}{4.18}$ per minute can be introduced, giving a rise of 5° per minute with the calorimeter described in Fig. 1. No ordinary calorimetric measurements would require that the jacket be heated up as fast as this. With pure water in the jacket the resistance is high and the heating correspondingly slow but small amounts of electrolyte diminish this resistance greatly. The amperage should be adjusted by the addition of dilute copper sulfate solution so that the rise in the jacket is appreciably more rapid than the most rapid rise in the calorimeter.

Corrosion with an alternating current is not great although the conductivity of the jacket becomes greater and greater, so that the solution must be changed at intervals. If the vessels become seriously corroded they may be renewed by electroplating.

By substituting a high-boiling liquid for water the range of the calorimeter may be extended beyond 100°. When a solution of ferric chloride in glycerol fills the jacket the calorimeter may be used up to 200°. In case the glycerol is pure it must be heated first as such a solution is a poor conductor at room temperatures. Experiments have shown that the adiabatic control here is just as satisfactory as with the aqueous solutions.

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[1] THIS JOURNAL, **37**, 1718 (1915).

Professor Derby has suggested (in conversation) the use of fused salts for electrolytically heated thermostats at much higher temperatures, and the same idea could be applied to calorimetry. In fact the use of such a calorimeter should open up a whole new field to accurate physical-chemical measurements.

Summary.

In conclusion it may be said that adiabatic calorimeters eliminate cooling corrections, thereby excluding errors from precision work and saving time in commerical work. They permit a slow and careful reading of a thermometer while the temperature is constant, and the taking of temperature before and after a determination becomes unnecessary.

Errors from evaporation are negligible in the Richards type of calorimeter or in the modification described in this article, as there is no colder matter in contact with the vapor; and heat can not be lost or gained from the room by conduction. For high temperatures, for slow reactions, or for large temperature differences, these calorimeters are absolutely necessary.

The description of an adiabatic calorimeter of new design is given and it has proved to be accurate and simple of operation.

The automatic control of this calorimeter by means of a selenium cell has been successful, and this very sensitive relay may find application in other work.

The calorimeter herein described is being used in this laboratory in the accurate determination of the specific heats of salt solutions and of organic liquids.

WORCESTER, MASS., April 29, 1916.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 269.]

THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.

BY JAMES KENDALL.

Received May 20, 1916.

1. Introduction.

The evaluation of the specific conductivity of pure water in equilibrium with the carbon dioxide of the atmosphere is a problem which is of especial importance in connection with the water correction in conductivity determinations.[1]

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[1] This subject will be discussed fully in a forthcoming communication.