

Thermodynamics of a Galvanic Cell

A physical chemistry experiment

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Theory

The relationship between the change in the Gibbs free energy of a system and the changes in entropy and in enthalpy is

$$\Delta G = \Delta H - T\Delta S$$

where G = Gibbs free energy (maximum useful work obtainable), H = enthalpy, S = entropy, and T = absolute temperature. The equation

$$\Delta G = -nFE$$

indicates the change in the Gibbs free energy for nF coulombs discharging through a potential E , where n = moles of electrons, and F = coulombs/mole of electrons.

Measurement of the potential of a galvanic cell at any given temperature will allow calculation of the maximum work obtainable from a given quantity of reactants, but a single potential measurement is inadequate to obtain values of ΔH and of ΔS also.

For a given galvanic cell

$$-nFE = \Delta H - T\Delta S$$

and, therefore,

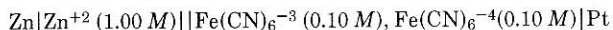
$$\Delta S = nF(\partial E/\partial T)_P$$

The change in entropy ΔS can thus be obtained from the slope at any given temperature of a plot of E versus T (1, 2).

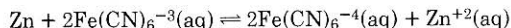
When ΔG and ΔS are known for a given T , ΔH is calculable.

Materials

The galvanic cell used was



The overall reaction was



The attractive features of this cell are the following.

- (1) The materials used in the cell are neither exotic nor expensive.
- (2) The potential is large (over 1 V), facilitating accurate measurement.
- (3) The $(\partial E/\partial T)_P$ is of the order of 10^{-3} V/°C, such that ΔS can be determined to two or three significant figures with even simple equipment.
- (4) Most of the entropy change of the system lies in the zinc half-cell such that a student can see the effects of entropy changes merely by being given comparison data on a Daniell cell— $(\partial E/\partial T)_P$ can be shown to be 100 times smaller for a Daniell cell (3), which also contains a zinc half-cell.

Experiment

The zinc electrode was a 1-cm wide strip of zinc sheet; the platinum was a tip electrode. A simple 0.1 M sodium chloride salt bridge was

used. The ferrocyanide-ferricyanide solution of potassium salts was made fresh as ferricyanide solutions decompose slowly upon standing.

Although a student potentiometer is adequate for potential measurement, as was noted in point three above, in point of fact a high impedance millivoltmeter (from Dattel) achieves near-reversible conditions and was used in this experiment.

Galvanic cell temperatures in the range 0°C to 55°C showed potentials of from 1.250 V to 1.150 V. These are certainly manageable with water baths and with even the simpler student-type potentiometers. It is useful here to recognize that the relatively large change of potential with temperature indicates some fairly good method of temperature determination. In this case, a mercury bulb thermometer accurate to a tenth of a degree Celsius was used.

Calculations

The E versus T plot was initially fit to the quadratic form

$$E = A + BT + CT^2$$

where A , B , and C are empirical constants. It turns out for this galvanic cell that C is three or four orders of magnitude smaller than B , such that to a good approximation (0.1% error) linear regression can be used to determine B ($= (\partial E/\partial T)_P$) from the form

$$E = A + BT$$

Pocket calculators with linear regression pre-programmed are readily available. Also, although less easily, one can perform a linear fit on the commoner types of pocket calculator. This possibility of using a linear fit to process the data is a nice feature not noted heretofore.

The equation relating E to T having been determined, several instructive thermodynamic calculations become possible. ΔG can be determined for any given temperature as can ΔS and then ΔH . Enthalpies of dilution (4, 5) are used to then convert ΔH to ΔH°_{298} ; activity coefficients are calculated (6, 7, 8) so that E°_{298} can be obtained from E_{298} . ΔG°_{298} and ΔS°_{298} are then calculable.

Acknowledgment

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