

relation between thermal and photochemical reaction. The black-body radiation from the vessel walls at zero degrees causes a rate of reaction which is negligible in comparison with that produced by radiation received from a body, emitting white light and not in equilibrium with the system.

2. Calculations from the reaction velocity constants at different temperatures give 24,700 calories for the critical increment, E . From the expression $E = Nh\nu$, λ is found to be 1.16μ . Light of this wave length, however, does not decompose nitrogen pentoxide within the limit of experimental observation.

3. Light in the region $400-460\mu\mu$ accelerates the decomposition of nitrogen pentoxide.

4. Nitrogen pentoxide is not decomposed by light between 400 and $460\mu\mu$ unless the dioxide is present.

5. The auto-catalytic effect of nitrogen dioxide is negligible in the dark.

6. Hypotheses to explain these facts are offered and their relation to theories connecting chemical action with radiant energy are suggested.

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OBSERVATIONS ON THE ZINC ELECTRODE.

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In a problem recently undertaken in this laboratory, it became necessary to measure small changes in concentration of zinc ion. As both the actual amount of zinc and the concentration changes involved were low (the former varying from the zinc contained in 10 cc. of 0.10 N zinc sulfate solution down to that contained in 10 cc. of 0.0025 N zinc sulfate solution, the latter varying by not more than a few per cent. of these amounts) it was thought that the zinc concentration cell might be used to accomplish the desired end.

A study of the literature, however, showed that all previous investigators had confined their attention either to dilute zinc amalgams of varying composition¹ and constant concentration of electrolyte, or to zinc amalgams or amalgamated zinc, with zinc salt concentrations not less than 0.5 N .² Moreover, in practically all instances it was found necessary to take some sort of precaution to prevent the access of atmospheric oxygen to the electrolyte, and to the electrode. Thus, Kistiakowsky,³ who worked with normal zinc solutions, found that constant potentials

¹ Richards and Forbes, *Carnegie Inst. Pub.*, 56 (1906).

² Mellenkamp, *Phys. Rev.*, 29, 329-50 (1909).

³ Kistiakowsky, *Z. Elektrochem.*, 14, 113-121 (1908).

could be secured by coating the electrode metal with paraffin, placing small pieces of zinc in the electrolyte and sealing the cell with paraffin oil. Richards and Forbes, in their research, protected the amalgams by using an atmosphere of hydrogen.

In the present work, which deals with the electrode potential of amalgamated zinc rods in solutions of zinc sulfate varying in concentration from 0.5 *N* down to 0.002 *N*, it was found that with cells of the Kistia-kowsky type, constant electromotive forces were impossible of attainment. In fact, only after considerable preliminary experimentation was it found that zinc electrodes reproducible at room temperatures to within ± 1 millivolt could be secured, by using well amalgamated zinc rods, and by bubbling hydrogen through the zinc half-cell during the measurements.

Indeed, unless these precautions are taken when electrodes containing 0.1 or 0.01 *N*, zinc sulfate are suddenly diluted to a lower concentration, the electromotive force may occasionally change in the wrong direction. If it is desired to study the electromotive force of such a "dilution cell," it is necessary to use water recently boiled, and at the same time carry out the dilution in such a way that at no time does air come in contact with the water used, after it has been boiled. This can easily be done, by fastening a buret into the stopper of the zinc electrode half-cell, filling with recently boiled water, and passing a stream of hydrogen through this water and through the half-cell previous to and during the dilution.

The measurements recorded below were made with observance of the above described precautions, using a Leeds and Northrup potentiometer, with a Weston cadmium cell as a standard. The zinc of a high degree of purity was kindly furnished by Mr. F. C. Breyer, of the New Jersey Zinc Company, Palmerton, Pa.

In Table I, the column headed "Obs. e. m. f." gives the observed values of electromotive forces for the combination: zinc | zinc sulfate | saturated potassium chloride | 0.1 *N* potassium chloride-calomel | mercury. It was intended to repeat the measurements when a constant temperature bath had been secured, but a change of employment of the writer has prevented this. Mellenkamp, in the article cited above, has shown that with an amalgam containing about 1% zinc, the temperature coefficient of the electrode potential of zinc is small, while the present work shows that changes of several degrees in temperature probably have only a slight effect. Accordingly, the measurements as given were made at "room temperature," which is given in each case. Each figure is a mean of at least 2 and generally several very closely agreeing measurements, made on half-cells assembled just before use.

The column headed "*E* obs." contains the electrode potentials of the zinc electrode at the concentrations given, on the basis of 0.3385 volt

for the 0.1 *N* calomel electrode, referred to the hydrogen electrode as a standard.¹

TABLE I.
Electrode Potentials of Zinc Electrode.

Electrode No.	Conc. <i>N</i> .	Temp. ° C.	Ob. e. m. f.	<i>E</i> obs.
19	0.5	21.3	1.1221	-0.7836
19	0.5	22.0	1.1220	-0.7835
20	0.5	22.0	1.1242	-0.7857
19	0.1	21.8	1.1387	-0.8002
19	0.1	22.9	1.1378	-0.7993
20	0.1	22.0	1.1386	-0.8001
20	0.1	22.6	1.1397	-0.8012
21	0.01	25.5	1.1614	-0.8229
22	0.01	20.8	1.1630	-0.8245
21	0.002	26.4	1.1793	-0.8408
22	0.002	20.1	1.1785	-0.8400

If we assume that the mean value for the 0.1 *N* zinc sulfate electrode is correct, and apply the Nernst electromotive formula $E = 0.0292 (\log C_1 - \log C_2)$ for concentration cells containing divalent ions, to the 0.5, 0.01 and 0.002 *N* cells, we get the values shown in the column marked "*E* calc." in Table II. There is considerable discrepancy between the observed and calculated values. If, however, we take into account the electrolytic dissociation of zinc sulfate, as shown in Table II, Col. 4,² we can calculate the electrode potential of the zinc electrode, not for the *total* salt but for the zinc ion at the concentration given. Doing this, we get the values shown in Col. 5, Table II. Applying the Nernst electromotive formula to these electromotive forces, and still using the 0.1 *N* zinc electrode as standard, we get the values shown in Table II, Col. 6. As is seen, the agreement is good.

TABLE II.

Conc. <i>N</i> .	Mean obs. <i>E</i> .	<i>E</i> calc.	α .	Obs. <i>E</i> ₁₀₀ .	Calc. <i>E</i> ₁₀₀ .
0.5	-0.784	-0.780	30	-0.769	-0.770
0.1	-0.800	-0.800	45	-0.790	-0.790
0.01	-0.824	-0.829	70	-0.820	-0.819
0.002	-0.840	-0.850	85	-0.838	-0.839

Summary and Conclusions.

1. Observations of previous workers are confirmed in that it has been found necessary to exclude oxygen as completely as possible in setting up zinc electrodes.

2. In the concentration ranges 0.5 *N* to 0.002 *N*, the method of coating the metal with paraffin, covering the electrolyte with paraffin oil and placing scrap zinc in the electrode cells, as advocated by Kistiakowsky, is insufficient to accomplish this end.

¹ Clark and Lubs, *J. Biol. Chem.*, **25**, 479-509 (1916).

² Jones and West, *Am. Chem. J.*, **34**, 357 (1905).

3. Electrodes reproducible to within ± 1 millivolt can be secured by making the dilute solutions with water recently boiled and cooled in hydrogen, the dilution taking place in an atmosphere of hydrogen, with the measurements being made while hydrogen is bubbling through the electrode vessel.

4. Using the precautions just described, the electrode potential of zinc in 0.5, 0.1, 0.01 and 0.002 *N* concentration of zinc sulfate have been measured at room temperature. Calculated values based on the electrolytic dissociation of the zinc salt and these measurements are in good agreement with each other.

5. The Nernst electromotive formula is applicable within the range quoted.

6. In order to measure very small changes in zinc-ion concentration, the zinc electrode even with the precautions described, is not satisfactory. Possibly dilute zinc amalgam electrodes, with extreme precautions for the avoidance of oxygen, would serve the purpose.

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THE CRYSTAL STRUCTURES OF THE AMMONIUM HALIDES ABOVE AND BELOW THE TRANSITION TEMPERATURES.

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Knowledge of the geometrical arrangement of atoms in crystals, which is now available as a result of X-ray crystal analysis, should lead to more definite conceptions of the shapes of atoms and the forces around them. In a recent paper¹ it was pointed out from considerations of atomic structure, that the ions of sodium, potassium, fluorine and chlorine should have cubic symmetry while the ammonium ion, like methane, should have tetrahedral symmetry. This conclusion was thought to receive support from the difference in the crystal structures of potassium and ammonium chlorides. The halides of sodium and potassium have simple cubic lattices such as would be expected if the crystals were built up of alternate cubical ions of alkali and halogen with their faces in contact. Each ion is surrounded by 6 equidistant ions of the opposite polarity. Bragg² found that the ions in ammonium chloride are arranged in a centered cubic lattice so that each ion is surrounded by 8 equidistant ions of the opposite polarity. It was suggested that the "tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to faces or corners of the tetrahedrons." It was pointed out that the

¹ Langmuir, *THIS JOURNAL*, **41**, 1547 (1919).

² W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," *London*, 1916, p. 158.