tion losses from oxide films coated on nickel rings. While less accurate than the data for nickel, the results are in agreement with the thermodynamic requirements for evaporation of nickel oxide, and yield 117,055 (±1000) calories for the heat of sublimation at the absolute zero. Allowance for some uncertainty in the ground state multiplicity of NiO vapor, and in molecular constants, increases the possible error limit by three to four kilocalories. The data yield the vapor pressure equation

$$\log p \text{ (atmospheres)} = -\frac{25{,}506}{T} - 7.67 \times 10^{-4}T + 7.21 \times 10^{-8}T^2 + 10.198$$

Absence of oxygen in the gases pumped from the sample during evaporation, and a comparison of the residual gas pressures in our apparatus with the dissociation pressures of NiO within the temperature range of our measurements, exclude any significant influence from NiO dissociation.

Evaporation of free nickel was little retarded by the presence of the oxide coatings ranging from 20,000 to 90,000 Å. in thickness.

Recent data on the heat capacity of nickel have been reviewed and values for the heat content, entropy and free energy function have been computed and tabulated. Tables of the free energy functions of NiO (solid) and NiO (vapor) are also included.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Vapor Pressures of Salt Solutions[1]

BY MAX F. BECHTOLD[2] AND ROY F. NEWTON

A convenient and accurate method for measuring the activities of water in salt solutions is very desirable in those cases in which it is difficult or impossible to obtain satisfactory measurements of the activities of the solute by electromotive force measurements. The method of Washburn and Heuse[3] modified by Gibson and Adams[4] and by Newton and Tippetts[5] appears to be quite promising, and has been further modified to increase both its accuracy and its convenience. Essentially the method consists of passing a gas successively through saturators containing pure water, an absorber, saturators containing the solution, and finally through a second absorber. Passing the same gas through both the pure water and the solution eliminates the need of measuring the gas. The vapor pressure of the solution can then be expressed simply in terms of the vapor pressure of pure water, the total pressure at each saturator, and the gain in weight of each absorber. In the older apparatus the pressure at the saturators varied, and it was necessary to read the pressures at frequent intervals during long runs in order to obtain reliable averages. The adaptation of relays for controlling the discharge pressure and the rate of passage of gas through the apparatus has made necessary only a single reading of each pressure. Slight condensation in the tubes connecting the saturators with the absorbers may produce serious uncertainties in the results, which has been obviated by enclosing the absorbers and connecting tubes in an air-bath just above the water-bath, maintained about five degrees higher than the latter, and at high humidity, thus preventing cooling due to evaporation at the point where the connecting tubes leave the water-bath. During preliminary adjustments the air-bath must be removed, and condensation may then occur in the connecting tubes. To avoid error due to collecting this condensate in the absorbers, a pair of "dummy" absorbers is connected in parallel with the weighed ones, and the gas is passed through them for about an hour after the air-bath has been adjusted. The establishment of steady flow conditions before the collection of water in the weighed absorbers also ensures that the same quantity of gas passes through both absorbers.

Apparatus and Materials

Measurements were made on solutions of barium chloride and of calcium chloride. The barium chloride solutions were prepared and analyzed as reported by Newton and Tippetts.[5] A sample of Mallinckrodt Analytical

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[1] Based upon a thesis submitted by Max F. Bechtold to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939. Presented at the Boston meeting of the American Chemical Society, September, 1939.

[2] Present address: du Pont Experimental Station, Wilmington, Delaware.

[3] Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915).

[4] Gibson and Adams, *ibid.*, **55**, 2679 (1933).

[5] Newton and Tippetts, *ibid.*, **58**, 280 (1936).

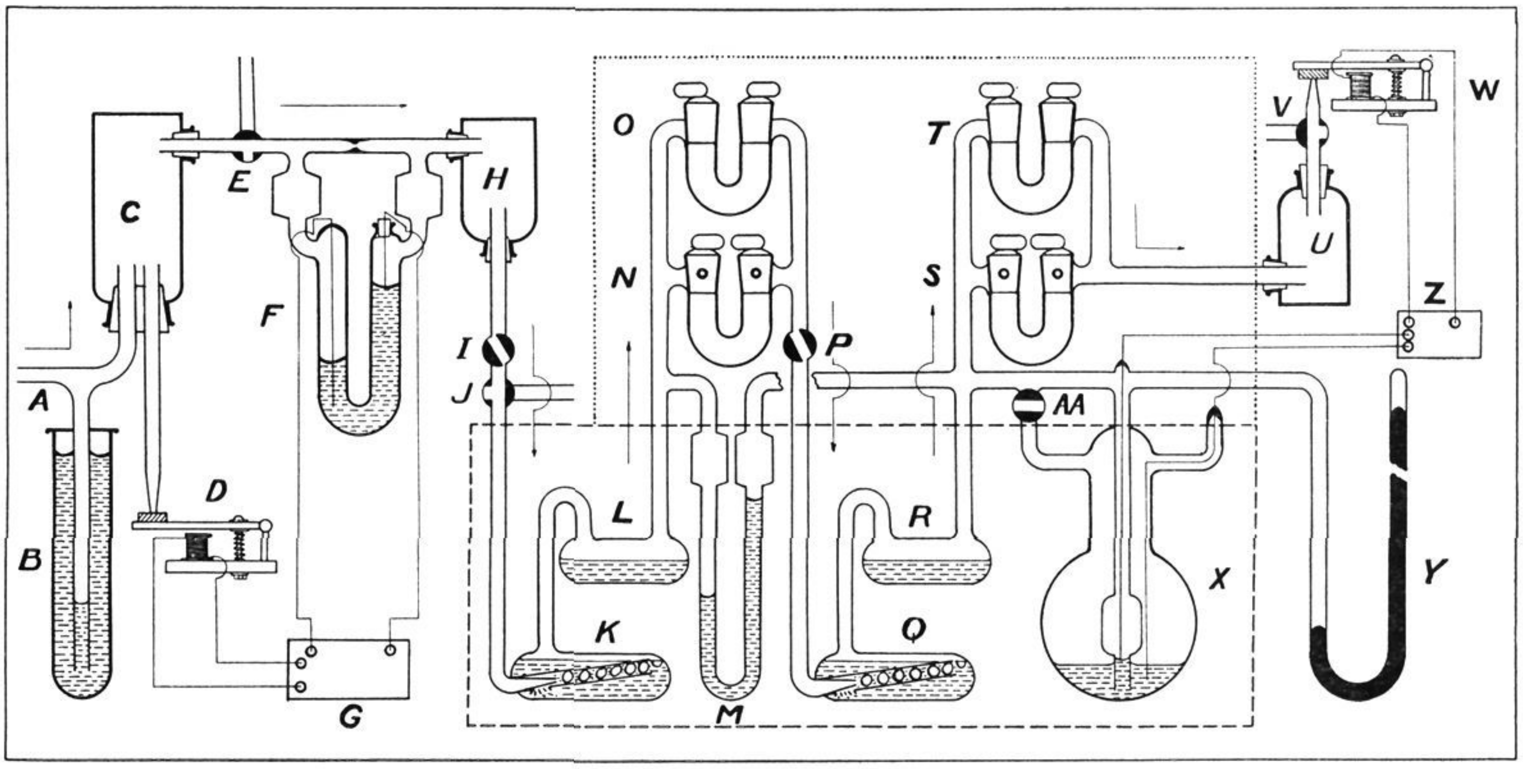

Fig. 1.

Reagent calcium chloride was found to contain only 0.12% of magnesium and alkali metal salts expressed as sulfates, and was judged sufficiently pure without recrystallization. The calcium chloride in the solutions was determined by adding a slight excess of sulfuric acid, evaporating, igniting, and weighing.

The final apparatus is shown diagrammatically in Fig. 1. The portion from A to J is a system for supplying the saturators with a stream of air at a uniform rate independent of atmospheric pressure and supply pressure. Air enters A at a rate in excess of that desired through the saturators. B acts as a safety valve which prevents the attainment of excessive pressures in case of accidental stoppage of the air stream. Flowmeter F maintains a constant rate through the saturators by controlling the action of magnetic valve D through the vacuum tube relay G. Dibutyl phthalate saturated with mercuric iodide is used as the manometer liquid in F because of its low density, negligible volatility and satisfactory electrical conductivity. Bottles C and H serve to smooth out pressure pulsations. The remainder of the apparatus is for the saturation of the air stream at a controlled temperature and pressure and for the absorption of water from it. The air stream passes into saturators K and L containing pure water, to absorber N or O, into saturators Q and R containing the solution being investigated, then through absorber S or T and out to the atmosphere. Throttling stopcocks I and P are necessary for satisfactory bubbling in the saturators. K and Q each represent a series of five similar saturators. It is necessary to place water in the first of the series Q because concentrated solutions crystallize in the jet of the bubbler and cause stoppage. The total pressures at L and R must be known in order to calculate the vapor pressure of the solution. The pressure at R is maintained constant within the accuracy of reading the barometer Y, by means of the regulator X which actuates the exhaust valve W through the relay Z. The conducting liquid used in X is the same as in F. The manometer M, which is filled with dibutyl phthalate, measures the difference in pressure between L and R. Previously it had been necessary to read M hourly because of change of porosity of the drying agent. This change is eliminated by using barium perchlorate in the left arm of each absorber and magnesium perchlorate in the right arm. The absorbers are completely refilled when the barium perchlorate is visibly wetted. The absence of clogging of the absorbers and the constant rate of gas flow make it unnecessary to read M more than once during a measurement. Only one reading of the barometer Y is required, whereas the hourly reading of a barometer and two manometers previously was necessary. The apparatus within the broken line is in a water-bath kept at 25, 35, or 45 ± 0.01°, while that within the dotted line is in an air-bath directly over the water surface. By the use of a small fan and a light bulb the air-bath was maintained about five degrees above the water-bath temperature and at about 85% humidity. These conditions prevent cooling the tubes which protrude from the water-bath. The stirring was such that no temperature difference between the bath around the upper saturators (K–L) and that around the lower ones (Q–R) could be detected by a Beckmann thermometer.

In places where flexibility is required, ends of glass tubing are joined by being butted together with neoprene tubing. Tests on these joints show no appreciable permeability to water vapor.

Procedure.—Assuming that the predetermined rate of flow has been set by adjusting the electrode in the right arm of F, air is started through A, and E is turned to connect C and F. The cocks of the "dummy" absorbers are opened, J is turned to connect H and K, and cock V is closed. When the pressure at R reaches a value not likely to be exceeded by the atmosphere, AA is closed and V is turned to connect U with the discharge tip controlled by W. After operating for some time, the air stream is diverted from the absorbers N and S to the

TABLE I

ACTIVITY OF WATER IN SOLUTIONS OF BARIUM CHLORIDE AND OF CALCIUM CHLORIDE

Molality	Activity at 25°	Probable error	Trials	Activity at 35°	Probable error	Trials	Activity at 45°	Probable error	Trials
				Barium chloride					
0.01017	0.99975	0.00009	7	.....	.....	...	.....	.....	..
.09505	.99608	.00004	5	.....	.....	...	.....	.....	..
.19087	.99151	.00006	4	0.99134	0.00012	4	0.99166	0.00008	5
.47231	.97866	.00007	12	.97830	.00005	4	.97834	.00011	7
.87460	.95774	.00008	4	.95831	.00010	6	.95874	.00016	10
1.23237	.93746	.00006	4	.93757	.00012	7	.93793	.00012	8
1.60010	.91483	.00011	5	.91460	.00008	4	.91493	.00006	7
				Calcium chloride					
0.3043	0.98633	0.00005	7	.....	.....	...	0.98705	0.00005	4
3.0335	.74583	.00010	6	0.74893	0.00006	6	.75256	.00029	5
7.0310	.30964	.00013	4	.32512	.00007	4	.34060	.00012	4

weighed absorbers O and T. The run is stopped by reversing all of the above operations.

Results

Measurements were made at 25, 35, and 45°, most of them on barium chloride, since comparison could be made with the activity calculated by the equations previously derived from electromotive force data.[5,6] The results are expressed in terms of the activity of water, assuming that

$$a_1 = p_1/p_0 \qquad (1)$$

and calculating p_1/p_0 by the equation

$$\frac{p_0 - p_1}{p_1} = \frac{m_0(B_0 - p_0) - m_1(B_1 - p_0)}{m_1B_1} \qquad (2)$$

in which p_0 and p_1 are the vapor pressures of pure water and solution, m_0 and m_1 are the weights of water evaporated from pure water and from solution, and B_0 and B_1 are the total pressures at the ends of the saturators filled with pure water and with solution, respectively. Equations (1) and (2) will be strictly true only if the gaseous mixture is a perfect gas, but as previously pointed out[5] the activity calculated by (1) and (2) is much less sensitive to imperfection of the gas than is either (1) or (2) itself, and the a_1 so calculated is almost free of error due to imperfection of the gas.

As a check on the apparatus, $(p_0 - p_1)/p_1$ was determined with pure water in both sets of saturators. The average of ten runs, some performed at each temperature, is +0.00014, with a probable error of the mean of 0.00008.

TABLE II

COMPARISON OF ACTIVITIES IN BARIUM CHLORIDE AT 25° BY INDEPENDENT METHODS

Molality	Activity from vapor pressure	Activity from e. m. f.	Difference
0.01017	0.99975	0.99950	0.00025
.09505	.99608	.99573	.00035
.19087	.99151	.99148	.00003
.47231	.97866	.97831	.00035
.87460	.95774	.95764	.00010
1.23237	.93746	.93739	.00007
1.60010	.91483	.91466	.00017

The number of runs under each set of conditions was varied according to the agreement of the results. When they were very consistent, as few as four runs were made, but when the consistency was not so good, runs were continued until it was judged that the mean was reliable. The "probable error" of the mean is given merely as a crude measure of the consistency of the results, since for so few cases the usual formulas give only the order of magnitude of the probable error. On very dry days difficulty was experienced in getting reproducible weighings of the glass absorbers, and in spite of the precautions taken to obtain reproducible conditions on the glass surfaces, it is believed that a large part of the chance error is due to error in weighing. It may be noted in Table II that all the differences are positive, which seems to indicate a systematic difference of about 0.02% between the two sets of measurements. In the vapor pressure measurements, the gas always passed first through the pure water. Some slight imperfections in the apparatus may lead to a small systematic error which could undoubtedly be reduced by carrying out half of the measurements with the solution in the first set of saturators.

Summary

An automatically controlled apparatus has been constructed for the precise measurement of vapor pressures of solutions by the dynamic method,

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(6) A typographical error is present in each of equations (5) and (6) of reference (5). In equation (5) the term beginning 0.34444 should begin with 0.034444, and in equation (6) the term 0.1349 m should be 0.01349 m.

and measurements have been made on aqueous solutions of barium chloride and of calcium chloride at 25, 35, and 45°. The activity of water in the barium chloride solutions changes only very slightly with temperature. The activity of water by vapor pressure measurement is in very good agreement with that calculated from electromotive force data, the maximum difference being 0.035%.

LAFAYETTE, INDIANA RECEIVED FEBRUARY 16, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Hydrogenation of Ethylene at Surfaces of Certain Oxides. I. Zinc Oxide and Zinc Chromite

BY JOHN F. WOODMAN AND HUGH S. TAYLOR

The measurement of the activity of oxides as catalysts for the hydrogenation of ethylene was originally undertaken in the expectation of checking the results of Vaughen and Lazier[1] on zinc oxide. These authors had reported negligible amounts of ethane resulting from the passage of hydrogen and ethylene over zinc oxide and other oxides at 400°. It was hoped that this absence of activity would be confirmed by a few preliminary runs, after which it was planned to investigate possible activity of zinc oxide for deuterium substitution, with a view to developing a convenient method for the production of deutero-ethylenes free from overwhelming amounts of the ethanes.

Unfortunately for this program, the preliminary runs showed that the ability of zinc oxide to catalyze the hydrogenation of the double bond in ethylene is far from negligible, even at temperatures much below those used by Vaughen and Lazier. Since the latter authors had made their results the basis of a rather inclusive hypothesis regarding the specificity of oxide catalysts for the hydrogenation of organic compounds, it seemed worth while to investigate the discrepancy more closely, and, if possible, to determine the factors responsible for it.

Lazier and Vaughen[2] themselves soon discovered the high activity of chromium oxide for the hydrogenation of the alkene bond and stated that this property set chromium oxide apart from other oxides. Turkevich[3] showed that ethylene introduced to a mixed manganese–chromium oxide catalyst at temperatures of 184° and above, underwent activated adsorption accompanied by decomposition, the products pumped off at higher temperatures being largely saturated hydrocarbons. This indicated activity for hydrogenation at lower temperatures than had previously been reported for chromium oxide catalysts. As a consequence of his observations, Turkevich pointed out that the specificity of oxide catalysts must be regarded as a matter of degree.

The discovery of the activity of zinc oxide and its thorough study led to test of the activity of zinc chromite. In a later paper[4] we report work on compounds of molybdenum, chosen because of the well-known industrial applications of the oxides and sulfides of this element in hydrogenation and cracking of oils and tars.

Experimental Details

Apparatus.—The apparatus used consisted of the following units: (a) a catalyst tube, at controlled temperature, isolated from the system by a trap kept at −78° to keep out mercury vapor; (b) a mercury manometer; (c) a pump system for evacuation; (d) burets for gas mixing and measurement; (e) purification trains for the gases.

Catalysts.—Zinc oxide was prepared from the oxalate by the method of Taylor and Sickman,[5] zinc chromite according to the method of Taylor and Strother.[6]

Gases.—Electrolytic hydrogen and tank ethylene, carefully purified, were employed.

Procedure.—Originally the gaseous mixtures were circulated by means of a Toepler pump over the catalyst in a closed cycle. The later determinations were made in a static system of conventional design with the catalyst at the bottom of a Pyrex cylinder of 35 mm. diameter and 250 cc. capacity.

Experimental Results

Zinc Chromite.—A mixture of 357 mm. of hydrogen and 198 mm. ethylene was admitted to 5.5 g. of catalyst at 21° and slowly raised in temperature to 215°, with frequent gas circulation.

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[1] Vaughen and Lazier, THIS JOURNAL, **53**, 3719 (1931).

[2] Lazier and Vaughen, *ibid.*, **54**, 3080 (1932).

[3] Turkevich and Taylor, *ibid.*, **56**, 2254 (1934).

[4] Woodman, Taylor and Turkevich, *ibid.*, **62**, 1397 (1940).

[5] Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[6] Taylor and Strother, *ibid.*, **56**, 586 (1934).