MASTER

FINAL REPORT

Submitted by
Indiana University
to
Atomic Energy Commission

A. E. C. Contract No. AT(11-1)-505

CHEMICAL EQUILIBRIA AT HIGH TEMPERATURES
AND THE MECHANISM OF VAPORIZATION OF COMPOUNDS

Principal Investigator
Ralph L. Seifert
Department of Chemistry

July 7, 1969

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and the Mechanism of Vaporization of Compounds

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Chemical Equilibria at High Temperatures
and the Mechanism of Vaporization of Compounds

PERSONNEL

- Dr. Ralph L. Seifert, Principal Investigator
- Dr. John Efimenko, Research Assistant from February 1, 1957, to January 31, 1959, received his Ph.D. degree in June 1962. His thesis was based on work done under this contract. He has been employed by the U.S. National Bureau of Standards since February 1959, studying high temperature vapor species by mass spectrometry. Work under this contract gave him experience with some of the experimental factors involved in his later work and developed his interest in the study of high temperature solid-vapor equilibria.
- Dr. Anthony F. Wilde, Research Assistant from February 1, 1957, to August 31, 1957. He later worked under Air Force Office of Scientific Research contract AF 49(638)-313, developing the electrochemical technique for studying formation equilibria of molten metal halides, which was later utilized in work under AT(11-1)505.
- Dr. Morris Bader, Research Assistant from February 1, 1957, to June 30, 1960, received his Ph.D. degree in June 1961. His thesis was based on work done under this contract. He entered academic work, teaching physical chemistry initially at Marietta College, Marietta, Ohio, and now at Moravian College, Bethlehem, Pa.
- Dr. Robert A. Prokop, Research Assistant from February 1, 1962, to February 28, 1963, received his Ph.D. degree in June 1963. Part of his thesis was based on work done under this contract. In February 1963 he accepted a research position with Minnesota Mining and Manufacturing Company.
- Dr. Theodore B. Warner, Research Assistant from February 1, 1962, to August 31, 1963, received his Ph.D. degree in September 1963. A large part of his thesis was based on work done under this contract. He served as a post-doctoral research fellow at the Naval Research Laboratory from September 1963 to September 1964 and has since been employed in a research position at the Naval Research Laboratory.
- Dr. Henry P. Longerich worked under this contract as a Research Assistant from February 1, 1963, to August 31, 1964, and then transferred to another research group. He received his Ph.D. degree in September 1967 and is now Assistant Professor of Analytical Chemistry at the University of Alaska.

Dr. Clyde R. Metz, Research Assistant from February 1, 1963, to August 31, 1965, and during July and August of 1966, received his Ph.D. degree in September 1966. His thesis was based on work done under this contract. He is now teaching at Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana.

Professor Clifford Shultz, then on the faculty at Evansville College, Evansville, Indiana, was employed as a full-time research associate from August 16 to September 15, 1965.

Mr. George Hahn, an undergraduate chemistry major, was employed as a part-time technician from April 1, 1959, to October 31, 1960.

Mr. John W. Brown, an undergraduate chemistry major, was employed as a part-time technician from January 21, 1964, to August 31, 1966. He has now completed his third year at the Indiana University Medical School.

OBJECTIVES

1. Development of techniques to determine the equilibrium partial pressures within a Knudsen cell of decomposition products that are gaseous at room temperature.

The Knudsen effusion method is a well-known technique that has been used for many years to determine vapor pressures of elements and compounds that are solid or liquid at room temperature and vaporize without decomposition. Development of techniques to determine the partial pressure within a Knudsen Cell of each decomposition product that is noncondensable at room temperature would permit experimental determination of the equilibrium constants for many decomposition reactions as a function of temperature and therefrom the calculation as a function of temperature of the thermodynamic quantities ΔG° , ΔS° , ΔH° for each decomposition reaction or its reverse, a formation reaction when decomposition is to the elements.

2. Determination of the feasibility of identifying the molecular species evaporating from a surface by measurement of the recoil of the surface.

The rate of weight loss resulting from the evaporation of molecules from the upper surface of a thin horizontal sample measured simultaneously with the recoil force on the sample provides sufficient information to determine the molecular weight of the evaporating molecules if only a single species leaves the surface and if the true surface temperature can be determined with sufficient accuracy. The experimental value of M is given by

$$M = 135.9 T \left[\frac{(dw/dt)}{\Delta w} \right]^2$$

where (dw/dt) is the weight loss by evaporation per second at surface temperature T and Δw is the apparent increase in weight of the sample produced by the recoil resulting from evaporation of molecules from only the upper surface of the sample. [Derivation of equation is given on page 7 of (1).] If several species, having molecular weights $M_1, M_2, M_3, \dots$, evaporate from the surface, the experimentally determined M corresponds to

$$M = \left(\frac{w}{\frac{w_1}{\sqrt{M_1}} + \frac{w_2}{\sqrt{M_2}} + \frac{w_3}{\sqrt{M_3}} + \dots} \right)^2$$

where w is the total weight lost by evaporation and $w_1, w_2, w_3, \dots$ are the weights lost as molecules with molecular weights $M_1, M_2, M_3, \dots$.

3. Further development and application of the electronic commutator method developed by Wilde and Seifert (2) for electrochemically studying formation equilibria of molten binary salts.

The electronic commutator method determines E° of formation cells by producing the constituent elements of the binary salt at the electrodes of a cell during electrolysis pulses. Analysis of the emf decay between pulses, with increasing cell current, permits determination of the reversible E° value. Advantages over the traditional reversible cell method are that: (a) temperature can more readily be maintained constant and uniform throughout the cell if nothing is introduced from outside the cell during measurements, as in the traditional reversible cell with gas electrodes, (b) proper behavior of the electrodes is constantly monitored by observation of pulse shape and emf decay curve, and (c) the size of the cell can be smaller than is feasible when a gas must be supplied at one electrode, as in reversible cells for molten halides. From determinations of E° of formation as a function of temperature, one readily calculates the thermodynamic formation constants ΔG° , ΔS° , ΔH° , and ΔC_p° as a function of temperature.

BRIEF DISCUSSION AND SUMMARY OF WORK IN EACH AREA

1. Determination of Decomposition Pressure of Nickel Oxide by the Knudsen Effusion Method.

Relative numbers of different molecules among the decomposition products effusing from a Knudsen cell can be estimated by mass-spectrographic techniques. The accuracy that can be achieved depends upon the accuracy with which the relative ionization cross sections of the different molecular species can be estimated and, when ion beam intensities are low, upon the accuracy with which the relative electron multiplier efficiencies for the various ions can be estimated. To convert to partial pressures, the same Knudsen cell is used with a stable substance of known vapor pressure, relative ionization cross section, and electron multiplier efficiency for its ions.

The determination of partial pressures within a Knudsen cell by collection, measurement, and chemical analysis of the effusing vapor is free of these experimental uncertainties and furthermore gives the equilibrium partial pressures directly. The purpose of this investigation was to determine whether techniques could be developed to accomplish such collection, measurement, and analysis of effusing decomposition products with sufficient accuracy to make this a competitive procedure for determining thermodynamic formation constants.

Prior to this study, the Knudsen effusion method was used by numerous investigators to determine the vapor pressures of metals and compounds vaporizing without decomposition. For most accurate results a collimated beam of effusing vapor was condensed on a target for a measured time and the amount of condensed material was determined by weight or radioactive assay to determine the weight of vapor condensed per unit time. To apply the Knudsen effusion method to the determination of noncondensable decomposition products and their equilibrium pressures in a Knudsen cell, it was necessary to develop techniques for collecting and analyzing gases in a collimated beam.

Unfortunately, the total planned investigation was not completed because the experimental procedures developed by Mr. Efimenko in the initial phase appeared too formidable to later graduate students, who therefore chose other research projects in the department. Fortunately, Mr. Efimenko was a careful experimentalist, skilled both in glass blowing and metal working. He was challenged by the problem, helped design and constructed the effusion and collection system and the micro-gas-analysis system used to measure and analyze collected gases. He tested the system and procedure by measuring the decomposition pressure of nickel oxide as a function of temperature. This oxide was chosen because considerable work had been published concerning the phase diagram for the Ni-NiO system [see (3)] and concerning ΔG° of formation of NiO as derived from thermochemical data and from studies of the reduction of NiO with hydrogen and with carbon monoxide by several investigators [see (4) and (5)]. The apparatus has been described on pages 1-3 of (6) and on pages 1-2 of (7). Some early results, obtained before sufficient knowledge had been gained to eliminate the effect of reaction of the NiO with the cell wall and before the procedure for collecting and effusing oxygen was perfected, were reported on page 3 of (1). Results of the final series of measurements were reported on page 2 of (7), but did not include the small correction for solubility of oxygen in molten nickel which has been included in the reevaluation of the work for this report. A detailed discussion of the apparatus, procedure, and results is given in (8). In the following summary, emphasis is placed on those aspects of the work in which other investigators may be most interested.

An alumina Knudsen cell, containing the NiO, was heated by radiation in a Pyrex chamber evacuated by two high-speed divergent-nozzle mercury diffusion pumps, each preceded by a cold trap. A collimated beam of the effusing vapor entered a collection chamber from which the noncondensable gases were pumped through two solid-CO₂-cooled traps by two mercury diffusion pumps and electrically controlled

Toepler pumps into the measuring pipette of a Prescott-Morrison micro-gas-analysis system (9) that was designed to analyze collected gas for water vapor, oxygen, carbon dioxide, hydrogen, and carbon monoxide. By means of mercury cut-offs, the collecting diffusion pumps could be exhausted to either the Toepler pumps or to 2-stage diffusion pumps used to evacuate gas collected from the collection chamber but not to be analyzed. When cell temperature had been held constant long enough to establish a steady state of pressures throughout the system, the exhausts of the collecting pumps were diverted for a measured time to the Toepler pumps and then back to the 2-stage diffusion pumps. Collection times of 10 to 30 minutes were used, which were sufficiently long to make negligible the error in the determination of the effective starting and stopping times.

In one series of measurements, the PV product for the total gas collected in an individual run varied from 2.04 torr ml (30 min collection with cell at 1590°K) to 9.32 torr ml (10 min at 1856°K), with oxygen contents of 9.70% and 75.84%, respectively. Background oxygen was determined by collecting gas from the collection chamber after a short period of evacuation of the system and with the cell at room temperature. The amount of oxygen thus obtained from the outgassing of the walls of the system was negligible compared to the estimated maximum possible experimental error in the PV product of oxygen collected during a run.

The Knudsen cell was fabricated from pure alumina by drain slip casting and the dried cell was sintered in vacuum at slowly increasing temperatures and finally held at about 2203°K for about 15 min. The shape of the cell was an inverted hollow cone the tip of which merged with a solid cylindrical stem that was supported on a 1 mm tungsten rod. The cell was closed at the top by a slip cast orifice plate with a conical orifice at its center. This plate was sealed to the top rim of the cell before sintering.

The cell was heated in vacuum during sintering and later measurements by radiation from a tungsten coil, wound to follow the contour of the sides and stem of the cell without touching it, and from a 0.05 mm thick tungsten ribbon, wider than the top of the cell and supported close to but not touching the top. A 2 mm diam. hole in the tungsten ribbon, concentric with the 0.7 mm cell orifice, permitted effusion of nickel oxide, nickel, and oxygen from the cell and also the sighting of the black-body cell interior with an optical pyrometer, whose readings were properly corrected for the transmissivity and reflectivity of the optical window at the top of the collection chamber and the silvered prism present in the optical path. Proper spacing of the windings of the tungsten coil provided uniform temperature of the cell body and its supporting stem, thus avoiding the cold spot opposite the orifice, which is apt to be present in cylindrical metal cells heated by induction. The independent temperature control of the orifice plate made possible adjustment of its temperature to be equal to or slightly greater than the temperature of the rest of the cell--i.e., the minimum temperature at which there was no condensation of nickel or nickel oxide at the orifice.

A cylindrical radiation shield, consisting of two spiral turns of 5 mil tantalum sheet surrounded by three turns of 5 mil molybdenum sheet, surrounded the tungsten heating coil. The radiation shield above the tungsten ribbon heater consisted of four parallel 5 mil tantalum sheets with proper holes to avoid interference with the vapor effusing in a solid angle considerably larger than that of the collimated beam to be collected. The gettering action for oxygen by the hot tungsten, tantalum, and molybdenum parts was essential for the success of the measurements. The resulting high pumping speed for oxygen in the Pyrex cell chamber was sufficiently large to make unnecessary a correction for oxygen entering the collection chamber from any source other than the collimated beam, which was defined by the opening between the two chambers. The gettering action is shown by the following. Just prior to heating a freshly filled non-outgassed Knudsen cell, the gas discharged by the mercury vapor pumps used to evacuate the cell chamber was collected for 30 min. For this sample at room temperature, $PV = 1.93$ torr ml, of which, 0.61 torr ml, or 32%, was water and oxygen. With the cell then heated at 1648°K , a similar collection for 10 min gave $PV = 8.52$ torr ml, of which, 0.28 torr ml, or 3.3% was water and oxygen. After this 10 min outgassing of cell and metal parts, collection for 30 min with cell and heaters at room temperature gave $PV = 1.45$ torr ml, of which 0.33 torr ml, or 23%, were water and oxygen.

Nickel oxide combines with alumina to form a blue spinel, $\text{Al}_2\text{O}_4\text{Ni}$. Early experiments showed that heating NiO in one of the Knudsen cells for three days at 1298°K in air produced no discoloration of the alumina and did not change the weight of the NiO . Repetition of the experiment at 1548° for one week produced a light blue coloration of the alumina where the NiO was in closest contact. When heated in vacuum to higher temperatures, a dark blue color was produced on the inside walls of the cell, penetrating to a depth of about 0.10-0.15 mm after prolonged heating. Constancy of repetitive measurements of oxygen effusing per minute at a constant cell temperature after some initial "seasoning" of the cell indicated that the activity of the NiO phase present in the cell was apparently not influenced by slow formation of additional spinel. Spinel formation provided a test for leaks in the Knudsen cell. Data obtained with one cell were discarded when, after the measurements, the blue color was observed on the outer surface along part of the seal between orifice cover and cell body, indicating leakage. The very narrow blue edge forming at the orifice did not observably influence the orifice diameter.

The final series of measurements, Table I, were obtained with a cell seasoned by filling it (through the orifice) with NiO and heating it in vacuum at high temperature until practically all the NiO had decomposed and effused or had combined with the alumina. The orifice diameter did not change during the "seasoning" or the subsequent reloading of the cell with NiO . After a preliminary heating at 1695°K for about 15 min, the data were obtained for runs 89-96, for which results are given in Table I.

TABLE I

Decomposition Pressures and Standard Free Energy of Formation of Nickel Oxide

Temp. (°K)	Run No.	P _{O₂} expt'l (atm)	P _{O₂} corrected (atm)	ΔG_f° (kcal/mole)	ΔG_f° Ref. (5) (kcal/mole)	ΔG_f° Ref. (4) (kcal/mole)
1590	89	$(9.12 \pm 2.4)10^{-7}$	$(9.04 \pm 2.4)10^{-7}$	-21.98 ± 0.43	-23.80	-22.34
1656	90	$(3.70 \pm 0.26)10^{-6}$	$(3.66 \pm 0.26)10^{-6}$	-20.60 ± 0.12	-22.49	-20.94
1700	94	$(8.47 \pm 0.32)10^{-6}$	$(8.38 \pm 0.32)10^{-6}$	-19.75 ± 0.06	-21.62	-20.01
1706	95	$(8.49 \pm 0.32)10^{-6}$	$(8.39 \pm 0.32)10^{-6}$	-19.81 ± 0.06	-21.50	-19.88
1710	91	$(6.95 \pm 0.43)10^{-6}$	$(6.86 \pm 0.43)10^{-6}$	-20.24 ± 0.11	-21.42	-19.58
1711	= Freezing point of nickel saturated with nickel oxide					
1764	92	$(2.66 \pm 0.08)10^{-5}$	$(2.63 \pm 0.08)10^{-5}$	-18.53 ± 0.05		-18.56
1801	93	$(5.33 \pm 0.14)10^{-5}$	$(5.24 \pm 0.14)10^{-5}$	-17.70 ± 0.05		-17.69
1856	96	$(1.41 \pm 0.05)10^{-4}$	$(1.38 \pm 0.05)10^{-4}$	-16.49 ± 0.07		-16.39

$$\Delta G_f^\circ = -(51,823 \pm 2,828) + (30.47 \pm 1.67)T - 3.68T \log T + 1.4 \times 10^{-4}T^2 - 1.0 \times 10^4 T^{-1}$$

$$\Delta G_f^\circ = -(59,937 \pm 1,711) + (2.354 \pm 0.955)T + 7.23T \log T - 1.36 \times 10^{-3}T^2 - 1.0 \times 10^4 T^{-1}$$

The third column of Table I gives the pressure of oxygen in the Knudsen cell, with the evaluation of "maximum" possible error for each determination. These pressures were calculated from the amount of effusing oxygen collected per minute, cell temperature, orifice size, and the fraction of gas effusing from an ideal orifice that will effuse in the solid angle defined by the cell orifice and the collimating aperture between cell chamber and collecting chamber. With this as a first approximation of the partial pressure of O_2 in the cell, the equilibrium partial pressure of atomic oxygen in the cell at each temperature was calculated by use of the dissociation constant of O_2 as given by Stull and Sinke (10). On the assumption that atomic oxygen effusing into the collection chamber was not trapped on the Pyrex walls but was collected as molecular O_2 , the fourth column in Table I gives the actual partial pressure of molecular O_2 in the Knudsen cell. In each run this correction was less than the maximum possible error in the determination of P_{O_2} .

Analysis of all the data obtained in earlier experiments and consideration of the work of others, as reported on pages 81-88 of (8), indicated (a) that a condensed nickel phase formed in the cell during measurements, because the vapor pressure of pure nickel at each experimental temperature is less than $2.71P_{O_2}$ [the pressure of $Ni(g)$ necessary for two atoms of Ni to effuse per molecule of O_2], (b) that the mutual solubilities of solid Ni and NiO were sufficiently small at the experimental temperatures to be negligible, and (c) that the solubility of oxygen in liquid Ni is not negligible, varying from 1.1 atom % at $1711^\circ K$ to 2.7 atom % at $1856^\circ K$ (11). It was therefore assumed that the activities of solid Ni and NiO were unity and the values of ΔG_f° in column 5 of Table I were calculated by the equation

$$\Delta G_f^\circ = 2.2878 \times 10^{-3} T \log P_{O_2} + 4.5756 \times 10^{-3} T \log x_{Ni}$$

where P_{O_2} is in atm and x_{Ni} is the mole fraction of Ni (1.00 below the freezing point of Ni).

The freezing point of nickel saturated with oxygen has been reported to be $1711^\circ K$ (3). A plot of the ΔG_f° values in Table I suggested that the value for the measured temperature of $1710^\circ K$ should be considered with those at higher temperatures, *i.e.*, that the nickel in the cell was probably supercooled liquid during most or all of the run, and that the equilibrium freezing point was possibly higher than $1711^\circ K$. Therefore the point was treated in this way in later calculations.

Columns 6 and 7 in Table I give values of ΔG_f° calculated for the experimental temperatures by equations given by Wicks and Block (5) and Coughlin (4). The equations for ΔG_f° below Table I were derived by accepting the same heat capacity data used by Wicks and Block (5) below the freezing point of the nickel and those used by Coughlin (4) above the freezing point of nickel. The two remaining constants in each equation (given in parentheses with their probable error) were

evaluated from the values of ΔG_f° in column 5 by the method of least squares, using weighting factors proportional to the reciprocal of the square of the "maximum" possible error in the experimental values of ΔG_f° .

2. Feasibility Study of a Recoil Momentum Technique to Identify Molecules Evaporating from a Surface.

Vapor effusing from a Knudsen cell has reached its equilibrium composition. The molecules present are those that left the surface of the solid or liquid phase present only if no reactions have occurred in the gas phase. However, it is possible that in some systems it is energetically more favorable for atoms or groups of atoms that are not adjacent in a solid to evaporate separately and then combine or otherwise react with each other in the vapor phase to produce the observed equilibrium composition. Searcy and Freeman (12) determined the molecular weights of tin and germanium by combining data from two types of vapor pressure techniques utilizing Knudsen cells. For each element they used a torsion system to measure the recoil force of two identical Knudsen cells to determine the pressure of the vapor phase inside the cells and, in separate experiments, they obtained the more customary weight loss data which is normally used to calculate the vapor pressure inside a Knudsen cell. Since the latter calculation requires use of the molecular weight of the vapor to evaluate the vapor pressure, use of the vapor pressure obtained by the torsion method permitted calculation of the molecular weight of the equilibrium vapor inside the Knudsen cells. They obtained molecular weights of 91 ± 29 for Sn and 58 ± 16 for Ge, whose atomic weights are 118.7 and 72.6, respectively.

By the Langmuir method the vapor pressure of a substance is calculated from its weight loss per unit of surface and unit time when free evaporation into a vacuum occurs. The calculation requires knowledge regarding the molecular weight of the vapor molecules leaving the surface and also of the condensation (or accommodation) coefficient for the vapor on the surface (usually assumed to be one). Whenever there is disagreement between vapor pressures obtained by the Knudsen and the Langmuir methods, the difference is usually explained by the lack of knowledge of the condensation coefficient, but in some systems it may be due to a difference between the molecular weights of atoms or molecules leaving the surface and those ultimately present in the confined equilibrium vapor. Combination of Langmuir-type weight-loss data with measurements of the recoil of the surface when molecules evaporate from it provides a means for determining the molecular weight of the molecules leaving the surface. The area of the surface and its condensation coefficient cancel, giving the simple equation already stated on page 2 of this report for the experimentally determined molecular weight. If a single species evaporates from the surface it will be easily identified by the molecular weight. If two or more species evaporate, their molecular weights and relative numbers will have to satisfy the equation for the average molecular weight given on page 3 of this report.

The large experimental errors in the high temperature measure-

ments by Searcy and Freeman (12) resulted primarily from difficulty in achieving uniform cell temperature in the torsion system. Achieving uniform temperature should not be a difficulty in the measurement of recoil of an evaporating surface in a vacuum. However, determination of true surface temperature may prove to be a difficult problem.

The apparatus that was designed, built, and used to test the feasibility of thus determining the species evaporating from a surface has been discussed briefly on pages 3-4 of (6), pages 4-5 of (1), and pages 3-4 of (13). Representative results with nickel samples were reported on pages 5-8 of (1) and pages 4-7 of (13). A detailed account of the work that was done in this laboratory has been given by Morris Bader (14). In the following summary, emphasis is placed on difficulties encountered and changes in apparatus and procedure that would have been made to decrease or eliminate these difficulties if work in this area had been continued. (The lack of facilities permitting some of the changes influenced the decision to discontinue this work and concentrate on the electrochemical study of formation equilibria.)

For the measurements completed in our feasibility study three materials were used: nickel, nickel oxide, and copper. The nickel was 5 mil foil of 99+% purity. The nickel oxide was oxidized 5 mil nickel foil, weight measurements indicating 99.5% conversion to the oxide. The copper was 7 mil foil of 99.998% purity. The samples, about $3/8$ inch square, were cut to fit in a square balance pan that was constructed from a $1/2$ inch square of 1 mil tungsten foil. Its inside dimensions were $3/8$ inch, with raised edges of about $1/16$ inch. It was suspended by 2 mil tungsten wire attached to its four corners and hung from a quartz microbalance by a 2 mil tungsten wire about 45 cm long.

The balance pan and sample were heated by radiation from an electrically heated 2 mil horizontal tungsten ribbon, $1/2 \times 2 1/4$ inches, which was parallel to the balance pan at a distance of 1-3 mm. Heating currents of 60 to 144 amp were required. The heater was approximately at the center of a 12 liter Pyrex flask, which was provided with optical windows for viewing the sample and determining the apparent surface temperatures of the sample and the tungsten ribbon with an optical pyrometer. The heater ribbon was surrounded by a radiation shield constructed of 5 mil tantalum foil. This was a rectangular box with an opening in the top for the balance pan.

This design made possible uniform heating of the entire sample surface. However, the light from the hot sample and from part of the heater was reflected onto the upper surface of the sample by the spherical glass surface of the sample chamber. Light from other portions of the heater was reflected onto the sample by the radiation shield. Of this reflected light, the portion reflected in turn to the optical pyrometer by the sample gave rise to high readings of "brightness" temperature and therefore high values of the surface temperature calculated by use of published emissivity values. That this source of error was significant was demonstrated by the fact

that during measurements with nickel at the higher temperatures, the observed brightness temperature of the nickel sample gradually increased although the heater temperature remained constant. During these runs a noticeable amount of nickel deposited on the inner surface of the upper part of the Pyrex chamber, increasing its reflectivity.

It should be possible to eliminate the above difficulty by using a water-cooled cylindrical metal vacuum chamber with a "non-reflective" inner surface and equipped with proper ports for lighting, observing, and manipulating interior components. If radiation shields are used about the heating ribbon, they should be designed so that no radiation from the heating ribbon can be reflected to the top of the sample.

The weight of the samples, when cold and while heated, was determined by use of a modified Honig (15) quartz microbalance. A detailed description of the construction and operation of the balance is given on pages 24-32 of (14). A 10-power telescope permitted detection of a pointer deflection of 0.01 mm, corresponding to a weight difference of 2×10^{-7} gm. The balance could handle loads of at least 500 mg. It was brought to its null point magnetically by manual adjustment of current in a solenoid acting upon a small magnet suspended from the balance. Load changes of 15 mg could be determined within $\pm 1 \mu\text{gm}$ from measurement of the solenoid current.

In this investigation the balance was brought to its null point only when a weight determination was made, which was for the cold sample at the beginning and end of the run and for the hot sample 6 to 8 times at approximately even intervals of 5 to 15 min. During the rest of the heating period the balance beam was allowed to rest on its fixed beam arrest. Therefore, during the short times of the weighings that determined the recoil of the sample pan owing to evaporation from the upper surface of the sample, the pan-to-heater distance was greater by a fraction of a millimeter than during the long periods between weighings in which practically all the loss in weight owing to evaporation was occurring. Although not detectable with certainty, there must have been a temperature difference in the two positions. The uncertainty in pyrometer setting was of the order of five degrees. Furthermore, while adjusting the balancing current to its correct value the vertical position of the balance pan changed.

Error from this variable sample position can be eliminated by designing a microbalance with movable beam support that will hold the beam in the null position between weighings or, preferably, by providing a means for automatic control of solenoid current so as to keep the magnetically controlled balance off the beam support and constantly at its null point. The latter would permit recording the weight constantly during a run so that evidence of any transient effects, otherwise unobserved, would be apparent. Mr. Robert Ensman of our laboratory has

designed circuits to thus control analytical balances, but no attempt has yet been made to adapt them to a vacuum micro-balance.

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The measurements at a given temperature consisted of a preliminary outgassing of heater, balance pan, and sample at the heater voltage setting to be used; then, in order:

- (a) The initial weight of the cold sample was determined.
- (b) The heater current was turned on at its predetermined value. The sample reached its equilibrium temperature in less than 1% of the total heating times used.
- (c) The brightness temperature of the heater ribbon and the weight and temperature of the hot sample were determined as a function of time from the turning on of the heater current.
- (d) The heater current was turned off. The sample cooled very rapidly to a temperature at which additional vaporization was negligible.
- (e) The final weight of the cold sample was determined.

Ideally, a corresponding blank run (without sample on the balance pan) under the same vacuum conditions, should be made before and after the sample run. Since the vacuum had to be broken and the heater chamber opened in order to transfer a sample to or from the balance pan in the apparatus that was used, it was impossible to be certain that blank runs were made under the same vacuum conditions or with exactly the same relative positions of balance pan and heater ribbon that prevailed during measurements with a sample.

Consequently in this investigation "blank" corrections were made by using a plot of correction term vs. heater temperature. The plot was based on a preliminary series of measurements made with empty balance pan at each of six heater temperatures, ranging from 1769°K to 2352°K. The following are observations during a typical run for which the heater temperature was 2270°K. At 178 sec after the heater current was turned on, the empty balance pan weighed 65 μ gm less than its final cold weight. Its weight gradually increased during the next 1090 sec, reaching a value 37 μ gm less than its final cold weight. The weight then stayed constant at this value during the remaining 500 sec of the heating period. This buoyancy effect was attributed to radiation pressure from the heating ribbon, which was constant during the heating period, and to the force of gas molecules impinging on the bottom of the balance pan during the outgassing of heater ribbon and radiation shield, which diminished as the metals became outgassed. The apparent weight decrease owing to radiation pressure was plotted as a function of the temperature of the heating ribbon. Proper buoyancy corrections for the measurements with samples were obtained from this curve.

On a plot of weight vs. time a perfect run with a sample on the balance pan is recognized by the fact that: (a) the final cold weight is less than the initial cold weight; (b) the hot weights lie on a straight line, within experimental error; and (c) extrapolation of

the "least squares" line determined by the hot weights gives intercepts at "current on" and "current off" times that lie the same distance above the initial cold weight and the final cold weight, respectively. The difference between the initial cold weight and the final cold weight gives the weight lost by evaporation during the measured heating time. When vaporization of the balance pan is negligible, as was the case with tungsten at the temperatures of our experiments, this weight difference divided by the total heating time gives dw/dt for the equation on page 2 of this report. The difference between hot-weight intercept and the corresponding cold weight gives the apparent effective "weight" of recoil owing to evaporation from the top surface of the sample. The true "weight" of recoil (Δw in the equation on page 2 of this report) is obtained by adding the radiation buoyancy correction for the heater temperature during the run. If sample, balance pan, heater, and radiation shield are not sufficiently outgassed prior to a run, the plot of hot weight vs. time is not linear at the beginning of the heating period and the data must be discarded. However, curvature may be present but not observed because of random error in the weight determinations, or buoyancy owing to outgassing of the heater may be partially offset by recoil owing to outgassing of the sample. Error will then result. It is to avoid this possibility that it would be desirable to obtain a blank run just prior to sample run (to insure proper outgassing) and following the sample run (to detect whether between runs there is sufficient gettering of gas molecules by the outgassed heater and radiation shield to produce an initial buoyancy error in the next run).

Therefore, in an improved apparatus it would be desirable to provide means for transferring the cold sample to and from the balance pan in vacuum. Then, "blank" measurements could be made under more nearly the same circumstances as the measurements with a sample on the balance pan and the possibility of error owing to outgassing could be ruled out by the observed data or an estimate of its maximum influence could be made.

Nickel was chosen for testing the feasibility of determining molecular weights of evaporating species by this method for three reasons. The probability is very small that the evaporating molecule is other than the atom of nickel and therefore it may be considered as a "known" sample. Its known volatility, ranging from 10^{-8} to 10^{-5} gm/cm² sec at temperatures from 1000 to 1500°K, was favorable for the apparatus that had been constructed. It provided an independent means for evaluating the temperature of the sample because Johnston and Marshall (16) had determined the rate of vaporization of nickel in a vacuum from a nickel cylinder heated by induction. The temperature of the nickel cylinder was determined by optical pyrometry. No emissivity corrections were necessary, because "black-body" holes in the cylinder were used. Assuming their temperature and mass loss measurements to be correct, we could utilize them to determine the temperature of our thin nickel sample from the observed rate of its evaporation.

In one series of measurements a small thin disc of graphite, 1/8 inch diam. by 0.01 inch (emissivity = 0.9), was placed on the

nickel sample. The relationship was determined between the brightness temperature of the graphite disc and the surface temperature of the nickel, as obtained from its observed rate of evaporation. The same graphite disc was later placed on a copper sample to determine the temperature of the copper surface, assuming that heat transfer from copper to graphite was the same at every temperature that it had been for nickel to graphite. An additional calibration point for the graphite disc was determined at the end of a run by gradually increasing the temperature of the copper until it melted.

Measurements were made at a total of 13 different temperatures, ranging from 1442-1595°K, using three different nickel samples. The values of M obtained in the various runs ranged from 9.6 to 193.8, giving an average value of 55.8 ± 30 , with a standard deviation of ± 47.7 , but only three measurements having positive deviation. In accordance with the statistical basis for rejecting an observation, the value 193.8 can be discarded with 99% confidence. The remaining 12 values, ranging from 9.6 to 96.7, give an average of 44.3 ± 24.6 with 5 measurements having positive deviation. Obviously the accuracy of these measurements is no greater than that reported by Searcy and Freeman (12) for the corresponding procedure involving effusion from Knudsen cells.

Of the twenty-five runs made with copper samples only twelve gave weight vs. time data for the hot sample that resembled a linear relationship sufficiently well to be used for an approximation of M . The resulting approximations varied from 1 to 561. If the two highest values, 561 and 294, and the two lowest values, 1 and 3, are disregarded, the remaining values lie in the range 6 to 37 with an average of 20.8 ± 10.2 .

The cold weights of each sample before and after heating should be more accurate than the weights determined while the sample is hot, because there is no radiation pressure or outgassing of surfaces nor is the weight changing during the weighing operation. The two cold weights provide a value for the vapor pressure of the metal if it is assumed that the molecular weight of the evaporating molecule is the atomic weight of the metal and that the condensation coefficient is unity. This has been done in the past to obtain the vapor pressures of metals by the Langmuir method. Vapor pressures thus calculated from the cold sample weights for the second and third of the four copper samples used are in general agreement with values interpolated at the same temperatures from values obtained by Marshall, Dorn, and Norton (17) using the Langmuir method. Agreement for the first and fourth samples was poor. This lack of agreement must have been due to errors in temperature measurement or factors in the preparation and handling of the samples whose influence was not recognized. Both the nickel and the copper samples had been abraded under carbon tetrachloride on No. 2/0 and 3/0 emery paper, successively, and then washed repeatedly in clean carbon tetrachloride and stored in it until they were used. The fourth copper sample was treated with hydrogen in a quartz tube at 300°C for four hours before it was abraded. A nonvolatile surface contaminant, while causing disagreement with the literature values of the vapor pressure by the Langmuir method because of its reduction of the area of evaporating surface, would not

influence M, because the effective surface area for weight loss and recoil would be the same.

Even though the weight loss data agree with values obtained by other procedures utilizing the Langmuir method for vapor pressure determination, the values obtained for M by the recoil method will be high if any outgassing of the heater ribbon occurs during the hot sample measurements. Since this could have occurred without detection in our apparatus, it may have been responsible for some or all of the abnormally high values of M.

Contamination of the heater ribbon that changed its emissivity would have no influence if the percentage change were the same for all wave lengths of light, which does not seem to be reasonable. If, after the calibration curve was obtained for the radiation pressure correction, contamination of the tungsten increased its emissivity at shorter wave lengths relative to its emissivity at the long wave lengths transmitted by the filter in the pyrometer, the contamination would have resulted in high values of M. If the relative emissivity at the shorter wave lengths was decreased by contamination, low values of M would have resulted. Unfortunately, additional radiation pressure curves were not obtained at intervals throughout the measurements here reported. Also, at the time the measurements were made, no thought was given to possible differences in the reflectivity of the bottom surfaces of replacement balance pans or to possible change in the reflectivity of a given pan throughout a long series of measurements.

The relatively simple apparatus used for this investigation was able to show that the recoil of a surface from which evaporation occurs can be measured and that it is possible to obtain a uniform temperature of the surface of a fairly large sample under conditions that permit measurement of the recoil force. Although the accuracy of measurement achieved was very poor, observations made during the work more clearly define the requirements for a more sophisticated apparatus that will permit a more accurate and broader study of the factors that must be considered in order to develop a procedure for accurately studying vaporization from surfaces at high temperature.

In spite of its shortcomings the apparatus was used for two series of measurements using nickel oxide samples in order to determine whether this technique might be employed to study decomposition reactions and also to determine whether it is essential that the balance pan be inert to the sample. When the pan is inert, vaporization or decomposition products from the bottom and sides of the sample will effuse from the area between the edges of the sample and the sides of the balance pan. In these experiments this area was less than 5% of the exposed surface of the sample. Effusion from this edge region will be similar to that from a Knudsen cell, since the effusing molecules may have had multiple collisions with the surface of the sample and with other gas molecules. Therefore the composition of the effusing gas may be different from that initially leaving the surface of the sample. The effective accommodation coefficient of the effusion area at the edges, like that of a Knudsen orifice, will

be near unity, whereas that of the free surface of the sample may be less than unity. If the composition of the effusing vapor is the same as that leaving the surface of the sample, no error will be introduced, since both the area from which vaporization occurs and the accommodation coefficient of the surface cancel in the derivation of the equation for M on page 2 of this report. However, if reaction occurs between the species that leave the surface or between the sample and the balance pan, an error will result if the reaction products are volatile at the temperature of the pan. The magnitude of the error will depend upon the ratio of the area between sample and pan edge to that of the sample, the volatility of the reaction products, the molecular weights of the products relative to those of the molecules leaving the top surface of the sample, and the accommodation coefficient of the sample surface.

In the first series of measurements with nickel oxide the sample was in direct contact with the tungsten pan. In the second series the sample was separated from the tungsten by a thin layer of zirconia powder, which is relatively inert to both nickel oxide and tungsten. Tungsten oxide, which is volatile at the temperature of the measurements, could be formed in the first series by reaction of tungsten and nickel oxide at the contact points between the two substances and could be formed in both series by oxygen atoms or molecules from the decomposition of nickel oxide diffusing to the hot tungsten surface. It had been hoped that elimination of direct contact by interposing zirconia would reduce the rate of reaction. The slight reduction in opportunity for reaction must have been offset by the fact that the balance pan and heater had to be at a higher temperature to achieve a given sample temperature. The first series had to be terminated after eleven runs at temperatures from 1483 to 1543°K and the second series after eight runs at temperatures from 1500 to 1589°K, because the balance pan began to swing violently. In each case a hole had developed in the bottom of the tungsten pan.

At the conclusion of the series of measurements, the surface of the second sample was a uniform light green, having changed during heating from its original black color. The first sample underwent the same color change but to a lesser extent. Both samples, which were nonmagnetic initially, were ferromagnetic after the heating in vacuum because of their free nickel content. The quantitative results were inconclusive. Fifteen runs gave sufficiently satisfactory data to permit approximation of a recoil "weight." Three runs gave very high values for M (118, 185, and 199). These occurred among the last half of the runs in each series, by which time some swinging of the balance pan was evident. The average value of M for the remaining twelve runs was 20.7 ± 31.7 . No value of M above 12 was obtained during the first half of the runs in each series. At most, the results are merely suggestive that initially the predominant species evaporating from the surface is atomic oxygen ($M = 16$). The increase of M in later runs no doubt resulted from the evolution of tungsten oxide between sample and balance pan edge and possibly through small holes in the tungsten pan. The latter would have a large effect because, in addition to increasing dw/dt in the equation on page 2, it would decrease Δw , whereas loss from the top of the pan increases Δw .

3. Determination of the Thermodynamic Formation Constants of Molten Metal Halides by the Electronic Commutator Method.

In accordance with the Proposed Technical Program submitted October 25, 1961, work under this contract after February 1, 1962, has been devoted exclusively to the electrochemical study of the formation equilibria of molten metal halides and related problems. The electronic commutator (or pulsed electrolysis) technique, developed by Wilde and Seifert (2) to determine E° of formation of liquid silver chloride, was further developed and used with a variety of halides to demonstrate that the procedure is capable of forming satisfactory reversible electrodes for chlorine, bromine, and iodine in the molten halides. An exhaustive series of measurements with lead chloride demonstrated that the precision and accuracy that can be achieved by this procedure exceeds that of most earlier work by the traditional reversible cell method, which required addition of halogen gas from a source outside the cell.

Theodore B. Warner rebuilt the electrical circuit used by Wilde and Seifert (2) to increase its precision and stability, and to provide greater range of current on-time and off-time. He also replaced the use of a gated amplifier to determine E as a function of time by the use of timed triggering of the oscilloscope. He applied the circuit in the measurement of E° of formation of lead chloride. His work has been reported on pages 1-7 of (18) and pages 1-13 of (19), and also in (20) and (21).

Robert A. Prokop, using a Dekatron-controlled pulsing apparatus which he had designed and constructed prior to working under this contract, studied the behavior of various graphite electrode designs when used in molten silver chloride. He studied the kinetics of the electrode reaction occurring at the chlorine electrode during charge and discharge and developed a design and procedure for making graphite electrodes that functioned properly for the electronic commutator procedure more consistently than those used previously. This resulted in a decrease in the percentage of prepared electrodes that have had to be rejected when tested and in a longer useful life for those that have the desired properties initially. His work has been reported on pages 7-15 of (18) and pages 12-18 of (19) and in (22).

Clyde R. Metz studied the application of the electronic commutator method to a number of different halides to determine whether satisfactory bromine and iodine electrodes could be produced by this method and to determine the influence, if any, of the solubility of metal in its halide upon the depolarization of the cell. He studied LiCl, AgCl, AgBr, AgI, and with John W. Brown, PbBr₂ and PbI₂. Lithium chloride has the highest melting point of these halides. Lithium is much more soluble in its molten chloride than are silver and lead in their molten chlorides. The work with AgCl, AgBr, and AgI included measurements on both isothermal and intentionally non-isothermal formation cells. The work by C. R. Metz has been reported on pages 2-9 of (25), pages 3-8 of (26), and pages 2-23 of (27) and in (28) and (29). The determinations of E° of PbBr₂ and PbI₂, by

C. R. Metz and J. W. Brown are reported for the first time in this report.

The Electronic Commutator Method. In the commutator method for determining E° of formation of molten binary salts, square-wave current pulses are passed between inert electrodes in the molten halide to form the constituents of a reversible cell. Pulsing cycles have ranged from 0.04 to 1.0 sec, with current pulse lengths of 0.008 to 0.25 sec. Cell emf is determined as a function of time between pulses. If satisfactory electrodes are formed, the overpotential decays rapidly, followed by a slow, essentially linear emf decay due to the decreasing activity of one or both reactants caused by diffusion from the electrode(s). The linear, diffusion-controlled portion of the emf decay curve is extrapolated to current-off time to obtain the reversible cell emf for the reactant activities at that time. Pulse current and/or pulse time are increased until a constant value is obtained for this extrapolated emf of the cell at 1 atm. This is E° for the cell if mutual solubilities are very low. If mutual solubilities of the elements and the salt are significant, proper corrections must be made by use of the Nernst equation. Observation of the shape of the emf decay curve and its change, if any, with time and with increasing pulsing current reveals whether the electrodes are functioning satisfactorily, whether maximum activities at 1 atm have been obtained, and whether convection currents that produce fluctuating electrode temperature are present in the cell. The cell signal, therefore, gives more information about the state and functioning of the cell than is available to one employing the conventional reversible cell method. Because no gas bubbles through the melt from an external source, it is easier to maintain a uniform cell temperature.

Studies of Graphite-Chlorine Electrodes in Molten Silver Chloride. In the early work by Wilde and Seifert (2) the graphite electrodes that were used for the chlorine electrode had an exposed surface of only 1-2 mm². The purpose was to decrease the current required to saturate the electrode with chlorine at unit activity during a short electrolysis pulse and ultimately to be able to use the method with small samples of salt. However, the overvoltage did not decay rapidly with about half the electrodes prepared and electrodes that initially functioned properly for this procedure frequently had to be replaced after a short period of use. Studies made by R. A. Prokop in molten silver chloride revealed the following.

The half-life for overvoltage decay at the silver electrode is always less than one microsecond. Therefore, the graphite-chlorine electrode is the source of the observed overvoltage of the cell following the electrolysis pulse. Graphite film electrodes, prepared with Aqua-Dag colloidal graphite, require only a small current density to obtain rapid saturation with chlorine, but the electrical contact at a graphite-tungsten interface such as he used deteriorates rapidly. The greater the area of contact of a graphite rod with the molten chloride, the less is the probability of encountering the "anode effect" and also the greater is the probability that the elec-

trode will function properly initially. Saturation of melt about the graphite with chlorine is facilitated by surrounding the graphite electrode by a hood or by a small chamber open to the melt by a small hole in the chamber wall. Overvoltage at the chlorine electrode decays very rapidly initially if the tips of the short graphite rods used to form the electrodes are pretreated by partial burning in an oxy-hydrogen flame. However, after a period of usage the voltage decay curves approach those characteristic of electrodes that were not thus pretreated. These observations were utilized in the design of electrodes used by Prokop (22), Warner (20), and Metz (28).

Characteristic emf-current and emf-time curves during and following the electrolysis pulse are given and discussed on pages 8-15 of (18), and pages 14-19 of (19), and pages 31-40 and 43-44b of (22).

Measurement of the overvoltage, η , at the chlorine electrode as a function of current, i , with two graphite electrodes of approximately equal area (I, 0.050 cm² and II, 0.055 cm²) permitted some tentative conclusions regarding the mechanism of the electrode reaction. Chlorine from an external source was bubbled through the melt at the chlorine-graphite electrode during these measurements. Plots of η vs. $\log(i + i')$, where i' is the experimental constant determined so as to give the best straight line for all the experimental points, had slopes agreeing with the equation

$$\eta = a + \frac{RT}{2F} \ln(i + i')$$

The constant a equaled 0.182 and 0.161 volt, temperature T equaled 793 and 791°K, and i' equaled 0.005 and 0.012 amp for electrodes I and II, respectively. The observed slope, $RT/2F$, rules out the possibility that the rate determining step in the electrode reaction is the discharge of chloride ions, which would result in a slope of RT/F . The experimental results are consistent with the equations that can be derived either by assuming the rate-determining step to be the diffusion of chlorine from the supersaturated region at the electrode surface or by assuming the rate-determining step to be the combination of Cl atoms to form Cl₂ molecules and also assuming that the surface coverage by chlorine is small and follows a Langmuir adsorption isotherm. Although the ratio of apparent areas of electrodes I and II was 0.91 the ratio of the effective areas of their active surfaces was about 0.42 as determined by the values of i' given above and also by the fact that the initial slopes of charging curves for electrode I were approximately twice those for electrode II. All the observations are consistent with the concept that the electrode reaction occurs at "active sites" that are increased in number by the partial burning of the graphite with an oxy-hydrogen flame and that can be destroyed or poisoned, making an electrode unsatisfactory for use in the commutator method for determining E° . During work with lead chloride it was observed that contact of a satisfactory graphite electrode with liquid lead that had accumulated at the bottom of the cell immediately poisoned the electrode. Even though chlorine was liberated at its surface for a long period of time, hopefully to remove all trace of lead, the graphite electrode continued to exhibit an overvoltage that decayed too slowly for use in determining E° .

Measurements with Lithium Chloride. The least satisfactory results thus far with the electronic commutator method were obtained in measurements with lithium chloride. Lithium chloride differs from the other halides used thus far in that it has the highest melting point, its reduced cation (Li) is more soluble in its molten chloride, and it causes devitrification of fused quartz at high temperatures. Since the experimental cell must be held at the temperature of the molten salt for prolonged periods of time, it was necessary to abandon fused quartz as construction material for the lithium chloride cell except for the electrodes, which could be easily replaced when necessary. A study of the nature of the action of molten lithium chloride on transparent fused quartz indicated that in the atmosphere of dry nitrogen used in these experiments there is no chemical reaction that would result in contamination of the melt. The devitrification under these conditions consisted only in formation of α -quartz, β -quartz, α -tridymite, and α -cristobalite in varying amounts, depending upon the thermal history of the sample. However, in the presence of water vapor lithium silicates ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, $\text{Li}_2\text{O} \cdot \text{SiO}_2$, and $2\text{Li}_2\text{O} \cdot \text{SiO}_2$) are formed. One experiment provided a cluster of pure crystals of $\text{Li}_2\text{O} \cdot \text{SiO}_2$, study of which resulted in a revision (23) of the previously accepted X-ray powder pattern for lithium metasilicate. It was observed that devitrification of the quartz can be retarded by protecting it with a coat of Aqua-Dag colloidal graphite. Boron nitride, alumina, and graphite crucibles were used to contain the lithium chloride inside an outer tube of alumina to contain the nitrogen or chlorine atmosphere. None of these materials were observed to react with lithium chloride, but the boron nitride spalled under the conditions of the experiment. No satisfactory results were ever obtained for E° of the lithium chloride formation cell. The major difficulty was attributed to electrode depolarization, which was accelerated by the higher temperatures and the greater solubility of the metal in the molten halide. However, there also seemed to be an abnormal amount of difficulty with electrode overvoltage. Time required for overvoltage to decay to a negligible value was longer initially and increased more rapidly with usage than was observed with the other halides. Cell resistance was often unexplainably high. The highest values of cell emf achieved were obtained during a run of short duration. After the first three measurements the cell resistance suddenly increased to 240 ohms after having been 21, 18, and 18 ohms during the first three measurements. Following are the values of observed cell emf, E , and corresponding values of E°_{calc} as obtained from thermochemical data (24).

$t^\circ\text{C}$	E	E°_{calc}
641.4	3.0684	3.549
696.7	2.7054	3.516
743.3	2.4275	3.489
798.1	2.3347	3.458

The above difficulties were not encountered in the work with the other halides.

Formation Cells for Silver Halides. Two identical hooded graphite electrodes were inserted in the molten halide, contained in a small alumina crucible under dry nitrogen maintained at 760 torr pressure in an outer tube of alumina. Precautions were taken to insure that both electrodes were at the same temperature during each measurement of the cell emf by the electronic commutator method. Three series of measurements were made involving use of AgCl from two different lot numbers and use of seven different electrode pairs. Fifty-six measurements of E° were made in the range 478.4 to 731.3°C. Three series of measurements were made using AgBr from a single lot number and using eleven different electrode pairs. Fifty-four measurements of E° were made in the range 447.0 to 742.9°C. Two series of measurements were made using AgI from a single lot number and using five different electrode pairs. Forty-four measurements of E° were made in the range 558.1 to 730.4°C.

The resulting "least-squares" equation for E° of each halide as a function of temperature is given by substituting in Eq. [1] the values of a, b, c, and W listed in Table II for each halide. $W \times 10^3$, as given in Table II for each halide is the difference between cell temperature, t, in °C and the value that was accepted as the melting point of the halide.

$$E^\circ (\text{volt}) = a - bW + cW^2 \quad [1]$$

The standard deviations of the experimental values of E° from the resulting equations were ± 0.7 , ± 0.8 , and ± 0.8 mv for AgCl, AgBr, and AgI, respectively. Values of E° calculated from the "least-squares" equations within the experimental temperature ranges have possible errors, based on a 99% probability limit, of ± 0.42 , ± 0.54 , and ± 1.10 mv, respectively. Equations for the derived thermodynamic formation constants ΔG° , ΔS° , ΔH° , and ΔC_p° are obtained by substituting the constants d, e, f, g, h, i, and W, given in Table II for each halide in the following equations.

$$\Delta G^\circ (\text{kcal/mole}) = -d + eW - fW^2 \quad [2]$$

$$\Delta S^\circ (\text{gibbs/mole}) = -e + gW \quad [3]$$

$$\Delta H^\circ (\text{kcal/mole}) = -h + iW + fW^2 \quad [4]$$

$$\Delta C_p^\circ (\text{gibbs/mole}) = i + gW \quad [5]$$

Values of E° derived from thermochemical data by Hamer, Malmberg, and Rubin (24, 30) differ as follows from these electrochemically determined values in the temperature ranges of their determination. Values obtained from (24) for silver chloride at 500, 550, 600, 650, and 700°C are greater by 0.5, 1.5, 2.5, 4.9, and 7.8 mv, respectively. Values given in (30) for silver bromide are greater at 450 and 500°C by 0.45 and 0.44 mv and are less at 550 and 600°C by 0.07 and 0.05 mv. The value given in (30) for silver iodide at 600°C is greater by 0.15 mv. These differences are all within the 99% probability error limits of the equations given by Eq. [1] and Table II. However, values for

TABLE II

Coefficients for Use in Eqs. [1], [2], [3], [4], and [5] To Calculate E° , ΔG° , ΔS° , ΔH° , and ΔC_p° of Formation for Liquid Silver Halides

$W \times 10^3$	AgCl	AgBr	AgI
	(t - 455)	(t - 432)	(t - 558)
a	0.9081 ± 0.00073	0.7997 ± 0.00075	0.5720 ± 0.00003
b	0.280 ± 0.015	0.288 ± 0.015	0.227 ± 0.026
c	0.110 ± 0.049	0.097 ± 0.044	0.220 ± 0.149
d	20.942 ± 0.017	18.442 ± 0.017	13.191 ± 0.0008
e	6.46 ± 0.35	6.64 ± 0.35	5.23 ± 0.60
f	2.54 ± 1.13	2.24 ± 1.01	5.07 ± 3.44
g	5.07 ± 2.26	4.47 ± 2.03	10.15 ± 6.87
h	25.64 ± 0.27	23.13 ± 0.26	17.54 ± 0.50
i	3.69 ± 1.65	3.16 ± 1.43	8.43 ± 5.71

Exptl.

range: $W = 0.023$ to 0.276 0.015 to 0.311 0.00 to 0.172

ΔG° given by Eq. [2] for AgCl (99% probability error limit of ± 0.010 kcal/mole or $\pm 0.05\%$ at 900°K) at the melting temperature, at 800°K , at 900°K , and at 1000°K , differ by -0.20% , -0.21% , -0.53% , and -1.39% , respectively, from the values given by Wicks and Block (5). Corresponding quantities for the other formation constants are: for ΔS° , Eq. [3] (± 0.3 gibbs/mole or $\pm 5\%$), 2.9% , 1.6% , 1.8% , and 3.3% ; for ΔH° , Eq. [4] (± 0.3 kcal/mole or $\pm 1.2\%$), 0.57% , 0.11% , -0.18% , and 0.15% ; and for ΔC_p° , Eq. [5] (± 2 gibbs/mole or $\pm 44\%$), -35% , -20% , -2% , and 13% . Similar comparisons for AgBr at its melting point, 800 , 900 , and 1000°K are: ΔG° (± 0.012 kcal/mole or $\pm 0.07\%$), -23% , -23% , -25% , and -26% ; for ΔS° (± 0.2 gibbs/mole or $\pm 3.5\%$), 20% , 16% , 18% , and 20% ; for ΔH° (± 0.2 kcal/mole or $\pm 1\%$), -14.4% , -14.9% , -15.3% , and -15.0% ; and for ΔC_p° (± 2 gibbs/mole or 50%), -21% , -0.3% , 15% , and 55% . Wicks and Block (5) give only estimated values for AgI.

Published values of E° for AgCl, determined by various investigators using the traditional reversible cell method, cover a range of about 13 mv at temperatures from 470 to 740°C . Three published equations for E° of AgBr, determined by the reversible cell method since 1930 , cover ranges of less than 130°C and differ among themselves by 4 mv, all giving higher values than Eq. [1] within their experimental temperature ranges. Two published equations for E° of AgI differ by 12 mv at 600°C and 7 mv at 650°C , both giving lower values than Eq. [1] within their experimental temperature ranges. These large variations in E° values determined by the reversible cell method

can be explained by temperature gradients in the cells, resulting primarily from introduction of halogen from an external source, and by depolarization effects under the conditions of some of the measurements.

To determine the magnitude of error possible owing to temperature differences between the electrodes, measurements were made by the electronic commutator method using a quartz U cell with an electrode in each arm of the cell. The temperature of one electrode, the reference electrode, was kept constant in each series of measurements as the temperature of the other electrode was varied. With the temperature of the silver electrode constant in the AgCl cell, the emf of the cell decreased by approximately 0.70 mv/deg increase in the temperature of the chlorine electrode. (The exact value depends upon the temperature of the reference electrode.) For AgBr and AgI cells the corresponding values are approximately 0.74 and 0.86 mv/deg, respectively. With the temperature of the halogen electrode held constant, the cell emf increased by approximately 0.38, 0.42, and 0.44 mv/deg increase in temperature of the silver electrode in AgCl, AgBr, and AgI cells, respectively. The difference between the two values for a given cell is related to the temperature coefficient of E° for the corresponding isothermal cell. If the two electrodes of a formation cell are at different temperatures but assumed to be at the same temperature, the magnitude of error in E will depend upon the temperature difference between the electrodes and the relationship of the measured cell temperature to the actual temperatures of the electrodes. For example, if the silver electrode in a conventional reversible AgCl cell is at the measured cell temperature of 650°C and the temperature of the chlorine electrode is only 630°C, cooled by the flow of insufficiently preheated chlorine, the reported cell emf will be high by 13.8 mv. If the measured cell temperature is 644°C, because of the temperature gradient in the cell, the cell emf reported for 644°C will be high by $13.8 + (650 - 644)(dE/dt) = 12.4$ mv.

Isothermal Formation Cells for Lead Halides: Lead Chloride.

Two graphite electrodes were inserted in molten lead chloride, contained in an alumina crucible under dry nitrogen maintained at 760 torr pressure in an outer tube of quartz. Provision was made to evacuate the cell chamber and to fill it with dry oxygen-free nitrogen, dry hydrogen chloride, or dry chlorine at 760 torr pressure. One graphite electrode, to function as the chlorine electrode, was hooded. The other, to function as a lead electrode, was enclosed in a small cylindrical quartz chamber having a small opening near the top. Certified reagent grade, assay 99.9%, lead chloride was treated to remove any oxygen and water and then heated for 30 hours at 525°C under flowing dry hydrogen chloride. Emf measurements were made with a purified nitrogen atmosphere except in one series of high temperature measurements in which the nitrogen was displaced by chlorine. At a total pressure of 760 torr the partial pressure of chlorine at the surface of its electrode was significantly less than 760 torr, owing to the partial pressure of the lead chloride vapor. Vapor pressure data by Barton and Bloom (31) were used to determine the partial pressure of the lead chloride and then the pressure of chlorine at each cell temperature. The observed cell emf was converted to E° by the Nernst equation. The resulting corrections ranged from 0.1 mv

at 552° to 47.8 mv at 904°C. No corrections were made for reduction in activity of the lead chloride at the electrodes by the solubility of lead at one electrode and chlorine at the other. Solubility data by Corbett and von Winbush (32) indicated that the correction at the lead electrode would be only 0.11 mv at 865°C, the highest temperature for which data were used to derive the equation for E° . The solubility of chlorine in lead chloride was not known. The E° values at 136 different temperatures in the range of 503.8 to 865.5°C were fitted to a polynomial in temperature by the method of least squares. An analysis of variance showed that terms through the fourth power were significant. This gave the following equation, including the standard error terms.

$$E^\circ(\text{mv}) = (1172.47 \pm 0.14) - (545.24 \pm 0.48) 10^{-3} (t - 675) + \\ (83.0 \pm 7.1) 10^{-6} (t - 675)^2 - (53.8 \pm 21.7) 10^{-9} (t - 675)^3 + \\ (1163 \pm 225) 10^{-12} (t - 675)^4$$

The standard deviation of the experimental points was 0.24 mv. Consideration of estimated maximum possible errors in temperature measurement and equality at the electrodes and of other possible systematic errors resulted in an estimated maximum possible error of E° , as calculated by the above equation, of ± 2 mv from 500 to 750°C and ± 3 mv from 750 to 870°C.

E° values reported by various investigators who used the traditional reversible cell method vary over a range of about 40 mv. The data reported by Artamonov (33) for the temperature range 535 to 643°C are within 1.2 mv of those found in this study. His primary purpose was to evaluate the suitability of the chlorine electrode as a reference electrode. Therefore, he controlled experimental conditions very carefully.

Values of ΔG° of formation, calculated from the E° equation for the temperature range of 800 to 1100°K agree with values reported in the JANAF tables (34) within 0.22 kcal/mole. Similarly for the other formation constants: ΔS° , 0.6 gibbs/mole; ΔH° , 0.56 kcal/mole; and ΔC_p° , 1.7 gibbs/mole.

Isothermal Formation Cells for Lead Halides: Lead Bromide and Lead Iodide. Measurements were made of the emf of formation cells of lead bromide and lead iodide in the same manner as those of the isothermal formation cells of the silver halides. Conversion to E° values was made in the same manner as for lead chloride by use of vapor pressure data by Bloom, Bockris, Richards, and Taylor (35) and Stull (36). The solubility of lead in lead iodide (37) at the maximum temperature of these measurements introduces a correction of only 0.04 mv. Therefore, no corrections were made for solubility of lead in molten lead iodide. It was assumed that the corrections for solubility of lead in lead bromide and of the halogen in each halide are likewise well within the experimental error of these measurements.

Values of E° and of the thermodynamic formation constants

ΔG° , ΔS° , ΔH° , and ΔC_p° , as derived from the "least-squares" equation for E° of each halide, are given by Eqs. [1] through [5] on page 21 of this report together with the expressions for W and the values of the constants a through i given in Table III. Analysis of variance of

TABLE III

Coefficients for Use in Eqs. [1], [2], [3], [4], and [5] To Calculate E° , ΔG° , ΔS° , ΔH° , and ΔC_p° of Formation for Liquid Lead Halides

$W \times 10^3$	PbBr ₂	PbI ₂
	(t - 373)	(t - 402)
a	1.1128 $\pm$ 0.0013	0.7391 $\pm$ 0.0016
b	0.639 $\pm$ 0.026	0.651 $\pm$ 0.021
c	0.131 $\pm$ 0.066	0
d	51.323 $\pm$ 0.060	34.088 $\pm$ 0.074
e	29.48 $\pm$ 1.20	30.04 $\pm$ 0.97
f	6.06 $\pm$ 3.04	0
g	12.13 $\pm$ 6.08	0
h	70.373 $\pm$ 0.777	54.371 $\pm$ 0.658
i	7.84 $\pm$ 3.93	0
Exptl. Range: $W = 0.000$ to 0.387		0.000 to 0.168

the data indicated that use of a quadratic equation was not justified in the case of the lead iodide. Therefore, E° of formation is represented by a linear equation and no value can be derived for ΔC_p° of formation of lead iodide. The standard deviation of experimental values from the equation for E° was 2.2 mv for the PbBr₂ and 2.4 mv for the PbI₂.

Values of E° derived by Hamer, Malmberg, and Rubin (30) from thermochemical data differ from these electrochemically determined values in the temperature ranges of their determination by a maximum of 12 mv. Values reported in (30) for lead bromide are less at 400, 450, 500, and 550°C by 6.6, 5.4, 2.8, and 0.8 mv, respectively, and those at 600 and 800°C are greater by 1.5 and 12.2 mv, respectively. Values reported in (30) for lead iodide are less at 450 and 500°C by 11.9 and 5.3 mv, respectively, and that at 550°C is greater by 1.2 mv. Thus, the two sets of values agree at about 570°C for lead bromide and about 540°C for lead iodide, with the value from thermochemical data for ΔS° of formation used with each halide being slightly greater (less negative) than that obtained from Eq. [3] and Table III.

Conclusion. Thus it has been demonstrated that the electronic commutator method can produce satisfactorily reversible electrodes for chlorine, bromine, and iodine, and that it is capable of providing accurate E° of formation values of chlorides, bromides, and iodides of metals that are only slightly soluble in their molten halides. Further investigation is required to develop a procedure for obtaining accurate data with halides of metals whose solubility is sufficient to cause depolarization errors with present procedures. Extension of the work with nonisothermal formation cells may give information regarding existence and magnitudes of potential gradients accompanying concentration gradients of dissolved metal and/or halogen in a molten halide. If such a potential gradient is significant but not determinable, it may be impossible to obtain accurate thermodynamic formation data from electrochemical data alone unless the solubilities of metal and halogen are low. Further investigation should also be made to extend the utility of the electronic commutator procedure to other binary substances, e.g., sulfides and oxides.

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Very little, if any, of this work could have been accomplished without the support received from the Atomic Energy Commission. This support has been greatly appreciated by the principal investigator, the Department of Chemistry of Indiana University, the Indiana University Foundation, and by each of the five students who, as a consequence of the support, were able to complete their work for the Ph.D. degree and gain the training in careful experimental research that today helps them make constructive contributions to science.

REFERENCES

- (1) Technical Progress Report C00-505-3 (Oct. 25, 1959).
- (2) A. F. Wilde and R. L. Seifert, J. Electrochem. Soc., 108, 1059-63 (1961).
- (3) M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd ed., McGraw-Hill, N.Y., 1958, pages 1024-6.
- (4) J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy, XII. Heats and Free Energies of Formation of Inorganic Oxides," Bur. Mines Bull. 542 (1954), pages 32 and 63.
- (5) C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements--Their Oxides, Halides, Carbides, and Nitrides," Bur. Mines Bull. 605 (1963), pages 84-5 and 106-8.
- (6) Technical Progress Report C00-505-2 (Oct. 25, 1958).
- (7) Technical Progress Report C00-505-5 (Oct. 25, 1961).
- (8) J. Efimenko, "Decomposition Pressure Measurements of Nickel Oxide at High Temperatures," Ph.D. thesis, Indiana University, June 1962 (available from University Microfilms, Ann Arbor, Mich., order no. 62-5030, 118 pp.).
- (9) C. N. Prescott and J. Morrison, Ind. Eng. Chem., Anal. Ed., 11, 230-3 (1939).
- (10) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," No. 18, Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1956, page 144.
- (11) H. A. Wriedt and J. Chipman, Trans. AIME, 203, 477-9 (1955).
- (12) A. W. Searcy and R. D. Freeman, J. Am. Chem. Soc., 76, 5229-32 (1954) and J. Chem. Phys., 23, 88-90 (1955).
- (13) Technical Progress Report C00-505-4 (Oct. 25, 1960).
- (14) M. Bader, "A New Recoil Momentum Technique for the Study of Mechanism of Vaporization at High Temperatures," Ph.D. thesis, Indiana University, June 1961 (available from University Microfilms, Ann Arbor, Mich., order no. 61-4419, 132 pp.).
- (15) J. M. Honig and A. W. Czanderna, Anal. Chem., 29, 1206-10 (1957).
- (16) H. L. Johnston and A. L. Marshall, J. Am. Chem. Soc., 62, 1382-90 (1940).
- (17) A. L. Marshall, R. W. Dornste, and F. J. Norton, J. Am. Chem. Soc., 59, 1161-6 (1937).

- (18) Technical Progress Report C00-505-6 (Oct. 25, 1962).
- (19) Technical Progress Report C00-505-7 (Nov. 10, 1963).
- (20) T. B. Warner, "Determination of E° of Formation of Molten Lead Chloride Using an Electronic Commutator," Ph.D. thesis, Indiana University, Sept. 1963 (available from University Microfilms, Ann Arbor, Mich., order no. 64-5505, 112 pp.).
- (21) T. B. Warner and R. L. Seifert, J. Phys. Chem., 69, 1034-9 (1965).
- (22) R. A. Prokop, "Electrode Processes in Molten Silver Chloride," Ph.D. thesis, Indiana University, June 1963 (available from University Microfilms, Ann Arbor, Mich., order no 64-505, 136 pp.).
- (23) C. R. Metz, "A Revised Powder Pattern for Lithium Metasilicate," Report C00-505-11 (Sept. 1965).
- (24) W. J. Hamer, M. S. Malmberg, and B. Rubin, J. Electrochem. Soc., 103, 8-16 (1956).
- (25) Technical Progress Report C00-505-9 (Oct. 25, 1964).
- (26) Technical Progress Report C00-505-12 (Oct. 25, 1965)
- (27) Technical Progress Report C00-505-13 (Oct. 29, 1966).
- (28) C. R. Metz, "Electronic Commutator Emf Measurements of Cells Containing Molten Silver and Lithium Halides," Ph.D. thesis, Indiana University, September 1966 (available from University Microfilms, Ann Arbor, Mich., order no. 67-3695, 95 pp.).
- (29) C. R. Metz and R. L. Seifert, "Emf of Isothermal and Nonisothermal Formation Cells of Molten Silver Halides," submitted for publication in J. Electrochem. Soc. [C00-505-14]
- (30) W. J. Hamer, M. S. Malmberg, and B. Rubin, J. Electrochem. Soc., 112, 750-5 (1965).
- (31) J. L. Barton and H. Bloom, J. Phys. Chem., 60, 1413-6 (1956).
- (32) J. D. Corbett and S. von Winbush, J. Am. Chem. Soc., 77, 3964-6 (1955).
- (33) B. P. Artamonov, "Collected Works on the Electrochemistry of Fused Salts," P. F. Antipina, ed., State Scientific-Technical Publishing House for Chemical Literature, Leningrad, 1940, pp. 31-9.
- (34) "JANAF Interim Thermochemical Tables," D. R. Stull, ed., The Dow Chemical Co., Midland, Mich., March 31, 1962.

- (35) H. Bloom, J. O'M. Bockris, N. E. Richards, and R. G. Taylor,
J. Am. Chem. Soc., 80, 2044-6 (1958).
- (36) D. R. Stull, Ind. Eng. Chem., 39, 517-50 (1947).
- (37) J. D. Corbett, S. von Winbush, and F. C. Albers, J. Am. Chem. Soc., 79, 3020-4 (1957).