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THE REACTION OF GRAPHITE WITH NITROGEN
and other pertinent thermodynamic systems studied
with a mass spectrometer*

J. BERKOWITZ

MASTER

Argonne National Laboratory, Argonne, Illinois

Final. 1962

The thermodynamic properties of a variety of refractory materials pertinent to nuclear reactor technology have been investigated in recent years by a technique involving a mass spectrometer as a tool for analyzing equilibrium vapor compositions. The basic experimental arrangement, described by Chupka and Inghram [1] in their early work, involves placement of the sample under study inside an oven which in turn is placed near the source region of a mass spectrometer. The oven is heated by radiation from an encircling filament and (for temperatures in excess of 1200°K) by electron bombardment. The vapor effusing from the oven is collimated by an adjustable slit before entering the ionization chamber, where it is ionized by a transverse electron beam of controlled energy. Mass analysis of the ions follows in a rather standard 60° -sector mass spectrometer, having a 12-inch radius of curvature.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

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If the mean free path of the molecules in the oven is larger than the diameter of the orifice, one may use Knudsen's equation to compute the rate of effusion of molecules as a function of pressure and temperature within the cell. Since one generally requires a range of operating pressure, and Knudsen's condition sets a maximum, this implies operation in a pressure range such that the mean free path is larger than the linear dimensions of the cell. Hence, since the utility of the Knudsen method is in large part dependent upon its assumption that equilibrium is established within the oven, one must require that the rate of approach to equilibrium be determined by a surface reaction. For this reason, it is generally desirable to maintain a large ratio of inner surface area to orifice area (ca. 100 to 1000). Among the variety of substances studied by this technique, those of particular interest as nuclear materials include boron [2] , uranium dioxide [3] , graphite [1] , and beryllium oxide [4] .

In this paper, we shall describe a variation of the above method which extends its application to another class of reactions. For illustrative purposes, let us consider the volatilization of lithium hydroxide. By analogy with the other alkali hydroxides which had been studied by the techniques described above [5], one might expect the following reactions:

However, in this instance another reaction,

is evidently [5] more probable than (1) and (2); indeed, when the basic mass spectrometric measurement described above was applied to the lithium hydroxide system, the evolution of a large quantity of water vapor obstructed the successful conclusion of the experiment. [5]

In order to study this system under more favorable conditions, a cell (Fig. 1) was designed at this laboratory [6] which permitted a controlled partial pressure of water vapor to react with crystalline Li_2O . This scheme allowed for independent control of reaction temperature and the pressure of evolved gas. With this additional degree of flexibility, it was possible to study the concentration dependence, and hence the thermodynamic changes (ΔH , ΔF°) associated with reactions (1) and (3). It was recognized that the attainment of equilibrium within the cell was somewhat more difficult with this technique so care was exercised in the design to require the vapor introduced into the cell to collide at least twice with a surface before being able to leave through the effusion orifice. Indeed, the average vapor species would have to make many more collisions with the interior wall of the cell.

One test of the approach to equilibrium in these experiments is to measure the same thermodynamic quantity in two fundamentally different ways. In the first, the equilibrium constant K_{eq} for any of the

reactions taking place (Eqs. 1-3 in the case of lithium hydroxide) is evaluated by identifying the measured ion intensities with their corresponding molecular concentrations in the oven, after applying appropriate calibration corrections. With this equilibrium constant, one may readily compute the standard free energy change ΔF° for the reaction being studied. If, in addition, one computes the entropy change in the reaction from known or estimated molecular parameters, the enthalpy change then follows from the well-known equation $\Delta F = \Delta H - T\Delta S$. This is often referred to as the Third Law Method.

An alternative method of measuring ΔH depends upon the rate of change of K_{eq} with temperature. The slope of the line obtained upon plotting $\ln K_{eq}$ vs $1/T$ is equal to $(-\Delta H/R)$, where R is the familiar gas constant. This approach to the measurement of ΔH is frequently termed the Second Law Method.

Since these two alternative approaches are truly independent, the former depending upon equilibrium compositions and the latter upon the variation of composition with temperature at the equilibrium condition, good agreement between the two methods provides reassuring evidence that equilibrium is being attained.

The molecular architecture of many molecules is still undetermined, and the Third Law Method cannot always be used as corroborative evidence. In those instances where molecular information is lacking, one

must estimate the appropriate parameters, and the resulting thermodynamic information is subject to considerable uncertainty. In the lithium hydroxide system described above, the necessary information for reaction (3) was available from previous experiments. For reaction (1) some estimates had to be made for the possible configuration of the gaseous LiOH molecule, introducing some error. In the case of reaction (2), however, the estimates concerning the structure and the 12 vibrational frequencies of the $\text{Li}_2(\text{OH})_2$ molecule introduced so much uncertainty that comparison with the Second Law Method was not very meaningful.

The experimental technique described above has also been applied to the study of the reaction corresponding to Eq. (4):

In this instance, there was sufficient experimental basis for reliably applying the Third Law Method. The value of ΔH_T obtained in this way, 41.3 kcal/mole, was in good agreement with the Second Law result [6], 42.3 ± 2 kcal/mole, thus supporting the assumption that the reaction was at equilibrium in the cell.

If more than one reaction is simultaneously occurring in the Knudsen cell, as is frequently the case, there is no assurance that equilibrium has been achieved for all if it has been attained for one. Each species

has its own characteristic rate of approach to equilibrium, which is often referred to as its accommodation coefficient. This parameter, too, may be a function of temperature.

These additional complications are illustrated below in the rather ambitious experiment that was directed at measuring the partial pressures of some hydrocarbon free radicals in equilibrium with graphite and hydrogen at ca. 2000°C. Of the radicals CH, CH₂, and CH₃ which we expected to observe, the thermodynamic properties of CH₂ were least known, and hence most interesting. They could be arrived at by studying the reaction

or the disproportionation reaction

If complete thermodynamic equilibrium were attained, any hydrocarbon gas introduced into the cell at an appropriate pressure and the indicated temperature should have given rise to the same concentrations of the various vapor species. In the actual experiments, it was found that the intensity of the CH₂⁺ ion, attributed to CH₂, varied considerably, which implied that equation (5) was not representing an equilibrium that existed under all conditions. On the other hand, the equilibrium constant for reaction (6) had a value of about 3.0 when H₂, CH₄, CH₃I, CH₂I₂, and C₂H₄ were

used as the source of hydrocarbons. In these experiments, the relative concentrations of CH , CH_2 , and CH_3 varied considerably. Hence, it appeared plausible, though not certain, that reaction (6) had attained equilibrium whereas reaction (5) had not. A tentative value of 86 kcal/mole for the heat of formation of CH_2 was obtained, assuming reaction (6) was indeed at equilibrium.

In an attempt to hasten the approach to equilibrium, a tiered Knudsen cell was constructed, and is seen schematically in Figure 2. Although this design was unable to provide more unambiguous results for the graphite-hydrogen reaction, it appears to have provided ample surface area for the attainment of equilibrium in the graphite-nitrogen system, which is the major topic of this dissertation.

The reaction of graphite with nitrogen is obviously of interest to nuclear technologists, working with graphite-moderated reactors which operate at elevated temperatures in the presence of nitrogen. In this reaction, the CN radical is expected to be a major product. The heat of formation of this species $[\Delta H_f(\text{CN})]$ and its dissociation energy $[D(\text{CN})]$ are related to the heat of sublimation of carbon, $L(\text{C})$, and the dissociation energy of nitrogen, $D(\text{N}_2)$, by the equation

$$\Delta H_f(\text{CN}) + D(\text{CN}) = \frac{1}{2} D(\text{N}_2) + L(\text{C}). \quad (7)$$

Until recently, there has been considerable controversy regarding the values

of $L(C)$ and $D(N_2)$, and thermodynamic information regarding CN was one approach used to deduce these quantities. Now there is general agreement concerning the values of both quantities on the right-hand side of Eq. (7), so that measurements leading to either $\Delta H_f(CN)$ or $D(CN)$ imply knowledge of both. Several different types of experiments have been employed to establish these values. In an excellent review, Gaydon [7] summarized the experimental situation as of 1950. At that time, Gaydon selected 7.6 eV for $D(CN)$ as the most probable value, based largely on two experiments. The first was an extrapolation of vibrational energy levels observed [5] in the CN spectrum to a convergence limit, which depended upon an uncertain interpretation of an observed predissociation. The second was based on the energy for onset of the process

which is related to $D(CN)$ via the relatively well-known heat of formation of C_2N_2 .

Subsequent to Gaydon's 1950 analysis, several different types of experiments were reported which disagreed with this value for $D(CN)$ but were more or less in agreement among themselves.

Brewer, Templeton and Jenkins [9] produced CN by resistance heating of a graphite tube in an atmosphere of nitrogen in a King-type furnace. By monitoring the emission of the $0 \rightarrow 1$ band of the Violet System of

CN as a function of temperature they hoped to measure $\log K_{eq}$ vs $1/T$ for the reaction

where CN^* represents the upper state of the Violet System. By subtracting the electronic and vibrational energy equivalent to the emission frequency, they could compute a heat of formation for ground-state CN radicals. This experiment resulted in a value of 94 ± 6 kcal/mole for $\Delta H_f^0(CN)$. It should be added that subsequent students in Professor Brewer's laboratory [10-11] have become aware of a systematic error in this type of experiment due to self-absorption by the emitting species. The value 109.5 kcal/mole for $\Delta H_f^0(CN)$ reported in the recent edition of Lewis, Randall, Brewer and Pitzer [12] is presumably based on a recalculation of the above experiment, taking account of the self-absorption errors.

Stevenson [13] studied the appearance potential of CN^+ from C_2N_2 and HCN, for which he obtained the values $20.3_1 \pm 0.2$ ev and $19.3_6 \pm 0.2$ ev, respectively. Combining these results with heats of formation for HCN, C_2N_2 and H_2 yielded for $D(NC - CN)$ the value 6.88 ± 0.2 ev, where Stevenson allowed for the possibility that the CN radicals are formed in excited states. He then measured the appearance potential of Cl^+ from $ClCN$, obtaining 17.81 ± 0.2 ev. Combining this result with the heat of formation of $ClCN$, Cl_2 and C_2N_2 , and the ionization potential of Cl yielded $D(NC - CN) = 6.92 \pm 0.2$ ev. Here again, Stevenson allowed for possible excitation in the CN

radicals produced.

Stevenson then argued that $D(\text{NC} - \text{CN})$ should be less than $D(\text{H}_2\overset{\text{O}}{\text{C}} - \text{CH}_2)$ since the C - C bond distance in cyanogen (1.36Å) is greater than that of a C - C double bond (1.33Å). He then proceeded to show that $D(\text{H}_2\overset{\text{O}}{\text{C}} - \text{CH}_2) \leq 5.6$ ev, using other electron-impact data. If he now assumed that the CN radicals formed on electron impact in each of his experiments can only be produced in the $A^2\pi$ state, containing 1.13 ev of electronic excitation, he must subtract this excitation energy in order to arrive at the dissociation of cyanogen into two CN radicals. Thus, Stevenson concluded $D(\text{NC} - \text{CN}) = 6.90 - 2(1.13) = 4.74$ ev, which does not violate the criterion he established involving $D(\text{H}_2\overset{\text{O}}{\text{C}} - \text{CH}_2)$. This is equivalent to $\Delta H_f(\text{CN}) = 91.5$ kcal/mole, or $D(\text{CN}) = 8.3_0$ ev.

McDowell and Warren [14] measured the appearance potential of CH_3^+ from CH_3CN , obtaining 14.6 ev. Combining this result with the ionization potential of methyl radical (10.08 ev) and $\Delta H_f^0(\text{CH}_3\text{CN})$ taken to be -19.8 kcal/mole they concluded that $\Delta H_f^0(\text{CN}) \approx 92$ kcal/mole. These authors rejected Stevenson's excited-state hypothesis, but considered the possibility of excess kinetic energy in the products of electron impact. These results pointed to a value $D(\text{CN}) \approx 8.35$ ev. Taking due cognizance of the new data, Gaydon [15] revised his analysis in 1953 to accommodate this value. In 1960 Herron and Dibeler [16] confirmed this result with some further electron-impact experiments. During the course of the present study, the results of some x-ray densitometry measurements of

shock waves in cyanogen mixed with krypton [17] yielded information supporting Gaydon's original interpretation and casting doubt on the results of the other experiments subsequent to 1950.

In the current experiments, using the techniques previously described, the Third Law Method was applied to the reaction

For reaction (9), there is very little uncertainty regarding the molecular parameters entering into the computation of ΔS° . On the other hand, the Second Law Method was difficult to apply. Although both the Third Law and Second Law Methods involve measurement of 3 ion peaks at a constant temperature and pressure, the latter requires a much greater precision in temperature measurement to arrive at an enthalpy result having comparable uncertainty to that attainable by the Third Law Method. Also, the accuracy of the slope method depends upon the range of temperature over which one can measure a reliable equilibrium constant, and practical considerations precluded operating over a range in excess of 250°C . Since in this instance the Second Law Method did not provide an adequate comparison for the results of the Third Law Method (the reverse of the LiOH case) two different "feed" gases, N_2 and C_2N_2 , were used on the assumption that equilibrium might be approached from opposite directions for reaction (9). The complete decomposition of C_2N_2 could be checked directly by monitoring the C_2N_2^+ peak

with the mass spectrometer as the temperature of the Knudsen oven was raised, and observing the diminution in ion intensity.

The results of the N_2 and C_2N_2 experiments, shown in Tables I - IV, are in good agreement with one another, leading to a value for $\Delta H_f^0(CN)$ of 109 kcal/mole, implying $D(CN) = 7.5 \pm 0.1_5$ ev. Most of the earlier experiments directed at determining this thermodynamic quantity by optical spectra, electron impact, thermal measurements, and shock-tube studies could be interpreted to agree with this result. In particular, Stevenson's [13] electron-impact data yield 7.2 ± 0.2 ev for $D(CN)$ if one merely rejects the excited-state hypothesis. This is in fair agreement with the present work. Similarly, the experiments of Herron and Dibeler [16], when divorced from the excited-state hypothesis adopted from Stevenson, yield for $D(CN)$ the values 7.29, 7.22, 7.96, 7.35, and 7.13 ev. In view of the apparent error inherent in the method, these values appear to be in good agreement with the present results. The correction to the spectral emission experiment of Brewer and coworkers [9] has already been mentioned. An unambiguous interpretation of the CN band spectrum is not yet available. If such an experiment is forthcoming, and if it is in general agreement with the $D(CN)$ reported above, it should provide a more precise value and close a most interesting, controversial and fruitful subject of physico-chemical investigation, the carbon-nitrogen system. A search was made for other possible azocarbon species up to C_6N_6 in this study; in all instances the corresponding ion intensities were at least ten times less abundant than CN^+ .

TABLE I. Significant changes in ion intensities as a result of the "shutter effect" (arbitrary units) in the nitrogen-graphite experiment. The measured temperature in this experiment, when corrected for the transmission of the pyrex window, was 2340°K .

Ion	Measured with 20 ev electrons	Corrected for ionization en- ergy above threshold	Corrected for relative ion- ization cross section	Corrected for relative effi- ciency of elec- tron multiplier
C^+ (mass 12)	3.63×10^4	3.63×10^4	3.63×10^4	3.63×10^4
N_2^+ (mass 29)	3.08×10^6	6.23×10^6	3.37×10^6	2.58×10^6
CN^+ (mass 29)	2.36×10^5	3.50×10^5	1.82×10^5	1.55×10^5

TABLE II. Significant changes in ion intensities as a result of the "shutter effect" (arbitrary units) in the cyanogen-graphite experiment. The measured temperature in this experiment, when corrected for the transmission of the pyrex window, was 2312°K .

Ion	Measured with 20 ev electrons	Corrected for ionization en- ergy above threshold	Corrected for relative ioniza- tion cross sec- tion	Corrected for relative effec- tivity of elec- tion multiplier
C^+ (mass 12)	2.20×10^4	2.20×10^4	2.20×10^4	2.20×10^4
N_2^+ (mass 29)	1.01×10^6	2.04×10^6	1.10×10^6	0.84×10^6
N_2^+ (mass 28)	1.82×10^8	3.68×10^8	1.99×10^8	1.52×10^8
CN^+ (mass 26)	1.65×10^5	2.45×10^5	1.27×10^5	1.08×10^5

TABLE III. Pressure calibration and derived thermodynamic quantities, based on data in TABLE I, for the reaction $\text{C(g)} + \frac{1}{2} \text{N}_2(\text{g}) \rightarrow \text{CN(g)}$.

Pressure calibration	$1.0 \text{ atm} = 2.11 \times 10^{12} \text{ units}$
Equilibrium constant	$330 \text{ atm}^{-\frac{1}{2}}$
$\Delta F^0(2340^\circ \text{K})$	-26.97 kcal/mole
$-\Delta \left(\frac{F^0 - E_0^0}{T} \right)$	-13.365
ΔE_0^0	-58.2 kcal/mole

TABLE IV. Pressure calibration and derived thermodynamic quantities, based on data in TABLE II, for the reaction $C(g) + \frac{1}{2} N_2(g) \rightarrow CN(g)$.

Pressure calibration	$1.10 \text{ atm} = 2.00 \times 10^{12} \text{ units}$
Equilibrium constant	$646^a \text{ or } 564^b$
$\Delta F^0(2312^0K)$	$-29.73^a \text{ or } -29.11 \text{ kcal/mole}$
$-\Delta \left(\frac{F^0 - E_0^0}{T} \right)$	-13.355
ΔE_0^0	$-60.6^a \text{ or } -60.0^b \text{ kcal/mole}$

^a Obtained by using mass 29 as a measure of N_2^+ .

^b Obtained by using mass 28 as a measure of N_2^+ .

LIST OF FIGURES

- Fig. 1. Leak-in oven.
Fig. 2. Tiered oven.

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GAS-INLET KNUDSEN CELL

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