vate corporation for the purpose of furthering nuclear chemical technology on the one hand, and basic research, in conjunction with the Southern universities, on the other. It is thus a microcosm in which are projected many elements of our modern American—and Southern—society.

Can such an experiment be made to work? It is important to remember that the national laboratory for nuclear research is a new species—that there are no blueprints for the successful national laboratory—and that there are probably several administrative setups that will prove to be workable. It has been stated that industry is not suited to manage a national laboratory dedicated in good measure to basic research—yet the experience of ORNL during the last year under Carbide management has demonstrated that first-rate basic research can be done in an industrial framework. One important reason is the fact that the subtle relations between staff and contractor have been so handled as to take into account the basic loyalties of the staff, which go primarily to the national laboratory rather than to the contracting agency.

Again it has been suggested that the successful national laboratory should be located close to a large city. Oak Ridge is rather isolated. But life in Oak Ridge and the other atomic cities has many attractive features. There exist cameraderie and opportunities to take active part in community and cultural activities which are quite beyond the prospect of the average city dweller. In large measure these features of life in Oak Ridge compensate for the cultural advantages of the large city—which so often are available but are left unused.

But it may be that the laboratory draws its essential strength from its position as the largest scientific institution in the South. It is commonplace to observe that the Southland is undergoing a modern industrial revolution—that living standards are increasing, and that, as a concomitant, a cultural rebirth is in the making. But the South has a long way to go, especially in the sciences. In making its influence felt throughout the scientific departments of the Southern universities, Oak Ridge National Laboratory, through the agency of the Oak Ridge Institute of Nuclear Studies, has a worthy educational mission to perform. Should it fulfill this mission then this fulfillment—this curious by-product of the atomic bomb—will almost surely rank in importance with any future technical advances which Oak Ridge National Laboratory—or any laboratory—can hope to achieve.

On the Calculation of Planet Temperatures From the Composition of Meteoritic Matter

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IN A RECENT PAPER, BROWN AND PATTERSON (*2*) STATE "the conclusion appears irrefutable that meteorites at one time were an integral part of a planet" similar in characteristics to the earth. The evidence for this conclusion which they emphasize especially consists of certain thermodynamic computations made on the basis of data which they have compiled. Careful analysis indicates, however, that even if we grant the assumptions involved in making these computations and even if we use the data assembled by Brown and Patterson, we should arrive at conclusions which are at variance with those proposed by these authors.

Brown and Patterson's thermodynamic calculations depend fundamentally on the assumption "that the observed distributions of elements [within meteorites] represent equilibrium distributions . . . [which] must have been established at temperatures of the order of 3,000° C and pressures of the order of 10^5–10^6 atms." The pressures specified depend, in turn, on the value assumed for the equilibrium temperature. It seems pertinent, therefore, to examine carefully the basis of the particular choice of temperature, and the degree of reliability of the value proposed.

The choice of 3,000° C as the equilibrium temperature is based on the correlations of data on equilibrium distributions between silicate and metal phases with the heats of formation of the oxides, in terms of the following *approximate* thermodynamic expression:

$$-RT \ln K \simeq \Delta H. \qquad (1)$$

The reliability of the calculated temperature depends, therefore, on the closeness of ΔH's for the formation of oxides and silicates respectively, and on the possible error involved in the use of equation (1).[1]

Adequate thermodynamic data on silicates are very sparse. There are, however, half a dozen cases yielding sufficient information (*1*) to make a comparison between the ΔH's calculated from data on the heats of formation of silicates and of oxides respectively. The pertinent information is summarized in Table 1.

TABLE 1

COMPARISON OF ΔH'S FOR REACTION (2) CALCULATED FROM HEATS OF FORMATION OF SILICATES AND OF OXIDES RESPECTIVELY

Silicate	$\Delta Hf - \Delta Hf_{FeSiO_3}$	Oxide	$\Delta Hf - \Delta Hf_{FeO}$	Deviation
Al_2SiO_5	− 350.2 kcal mole^{-1}	Al_2O_3	− 315.7 kcal mole^{-1}	− 34.5 kcal mole^{-1}
$BaSiO_3$	− 89.5	BaO	− 68.7	− 20.8
$CaSiO_3$	− 104.4	CaO	− 87.4	− 17.0
($FeSiO_3$)	......	(FeO)	......	.....
$MgSiO_3$	− 74.0	MgO	− 81.8	7.8
$MnSiO_3$	− 27.8	MnO	− 32.2	4.4
Na_2SiO_3	− 97.7	Na_2O	− 35.2	− 62.5

Even if we omit consideration of the case of Al, since there may be some doubt as to just how to correct the silicate data for the difference in valence states, it is apparent that differences from 4 to 60 kcal can be encountered. These deviations would have a profound effect on the calculated temperature, as will be indicated shortly.

The method used by Brown and Patterson (*2*) to obtain 3,000° C as their estimate of the temperature depends on the validity of equation (1). They have recognized, as have all physical chemists, that implicit in the use of this equation is the assumption that entropy changes in the reactions considered are negligible. Practically no reliable data are available to examine this assumption in the present systems.[2] In the absence of information on entropy changes, *equation (1) can be relied upon only for large ΔH's,* especially when the reactions considered occur at elevated temperatures; *yet Brown and Patterson find agreement with a temperature of 3,000° only for data with small values of ΔH,* as is apparent from their figure 3 (*2*). The method of presentation which they have used, however, tends to obscure the magnitude of these deviations. An enlightening insight into the seriousness of these discrepancies can be obtained from the following considerations.

From the data compiled by Brown and Patterson, it is possible to calculate temperatures for each of 16 reactions of the type

$$M + FeSiO_3 = MSiO_3 + Fe \qquad (2)$$

if one uses equation (1) and the oxide ΔH's. It is a significant coincidence that, on the whole, the higher the ΔH the higher the temperature (see Table 2); in other words, the more nearly one approaches a region where equation (1) is likely to be reliable, the higher the calculated temperature. For the Ca reaction, with the highest ΔH, T becomes 7,600° K. Furthermore, if the silicate enthalpy data are used instead of the oxide data, T becomes 9,200° K in the calcium case. Since entropy data are lacking, the correct answer may be even higher. Even an exceedingly conservative estimate for ΔS of only 1 cal mole^{-1} deg^{-1} makes a temperature in the neighborhood of 10,000° K highly plausible. In any event, one is forced to the conclusion that an estimate of 3,000° is based on the

TABLE 2

TEMPERATURES CALCULATED FROM HEATS OF REACTION FOR OXIDES

ΔH kcal/ mole O atom	T °K	ΔH kcal/ mole O atom	T °K
4.1	− 1,580	− 7.8	3,320
19.3	6,450	− 8.2	2,700
23.6	2,650	− 13.2	4,950
23.6	2,620	− 30.7	5,000
25.1	2,960	− 48.7	6,900
35.3	3,400	.....	....
39.3	4,900	.....	....
43.3	5,200	.....	....
67.3	4,200	.....	....
78.3	4,800	.....	....
86.3	7,600	.....	....

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[1] The propriety of using thermodynamic data obtained at temperatures near 300° K to draw conclusions about processes which occurred at temperatures from 10 to perhaps 30 times greater also requires critical comment. This aspect of their computations is not clearly dealt with by Brown and Patterson; nevertheless, it will not be pursued further in the present communication.

[2] K. K. Kelley (*3*) has reported standard entropy values of 16.2 and 21.3 cal mole^{-1} deg^{-1} for $MgSiO_3$ and $MnSiO_3$ respectively, at 298° K. Thus a ΔS of 5 entropy units occurs in at least one known case. Even at 3,000°, the additional uncertainty due to the neglect of ΔS thus becomes at least 15 kcal.

least reliable region of the data available,[3] and that the most justified use of equation (1) leads to considerably higher temperatures.[4]

Since there can be little doubt that the assumed temperature of equilibrium of 3,000° is far too low, we can turn attention to the pressure calculation. The basis of the estimate of 10^5 atm is the deviation between zur Strassen's experimental equilibrium constants and those calculated for the meteoritic matter. By assuming that temperature changes make no significant contribution, Brown and Patterson calculate that pressures of 10^5 atm could produce the difference. This calculation is correct in principle if we grant the assumption that there is no significant difference between zur Strassen's laboratory temperature of about 1,800° K and that in the planet of origin of the meteorites. However, it is quite clear from the preceding remarks that the temperature at which equilibrium was attained (if indeed the process is an equilibrium one) is substantially higher than 1,800°. Just how much higher it need be, to satisfy the fortyfold increase in equilibrium constant, cannot really be said. We might use the van't Hoff relation for the temperature dependence of the equilibrium constant, but the necessary integration can be carried out only with the additional assumption that ΔH does not change over a temperature interval of several thousand degrees, an assumption which is most hazardous, particularly if we approach a temperature region where the metals begin to vaporize.

The second argument which Brown and Patterson introduce to justify the acceptance of a pressure factor is again highly questionable. In considering the reaction

$$M + FeS = MS + Fe \qquad (3)$$

they find, in contrast to the silicates, no correlation between the equilibrium constant and ΔH. In proceeding to explain this apparent anomaly, they point out that the heats of formation of metallic sulfides are considerably lower than those of the corresponding oxides. From this observation, they make the unwarranted conclusion that ΔH for reaction (3) " will be generally considerably smaller" than ΔH for a reaction of the type of (2). Such a conclusion is itself unjustified, because ΔH for either (2) or (3) measures a *difference* in heats of formation, so that if both MS and FeS have enthalpies of formation equally less than those of the corresponding oxides, ΔH for reaction (3) would be the same as that for reaction (2). Actually, the two ΔH's run very nearly parallel, as estimated from data in Table 6 of Brown and Patterson. In four out of seven cases the *difference* is less than 5 kcal, in two less than 13 kcal, and only in one as high as 19 kcal. With the possible exception of the single value of 19 kcal, ΔH for reaction (3) is not "generally . . . considerably smaller" than that for (2). The differences are well within the most conservative estimates of the unreliability of oxide data for estimating ΔH's of silicate reactions.

It is true, however, that the absolute values of the ΔH's for the sulfide reactions calculated *for the limited number of systems considered* by Brown and Patterson are small, (between -12 and $+23$ kcal), but so are the ΔH's for the corresponding oxide systems (between -31 and $+20$ kcal). In fact, it should follow, since the best correlation between equilibrium constants and ΔH's in the oxide system was obtained for small ΔH's, that the sulfide systems should also show a definite correlation. Actually, as the authors point out, no significant correlation is evident.

From the remarks which have been made above, in connection with the reliability of equation (1), it is not particularly surprising that the equilibrium constants for reaction (3) are not related to the ΔH's; for this is an excellent example of a case where equation (1) cannot be expected to be valid, since the ΔH's are small. Hence, the introduction of the pressure factor to explain the lack of correlation in the sulfide systems is definitely unwarranted, for the lack of correlation is exactly what one should expect when an equation is applied under conditions which do not fulfill the postulates used in its derivation.

A similar procedure applied to any one of many common series of reactions produced in the laboratory under atmospheric pressure would lead one to the contradictory conclusion that pressures of many atmospheres had been used.[5]

Thus, it is apparent that the arguments proposed for the assumption of pressures near 10^5 atm cannot

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[3] The unreliability of data in the region of small ΔH's is shown forcefully by the *negative* absolute temperature (see Table 2) obtained for a ΔH of 4.1 kcal.

[4] It should be pointed out, in addition, that temperatures calculated from large equilibrium constants, corresponding to large ΔH's, are more reliable than those calculated from small equilibrium contants, corresponding to small ΔH's, because of the logarithmic nature of the function relating K and T [see equation (1)]. Thus, for a K near 4×10^3 (Brown and Patterson's highest value), a tenfold error (i.e. 1,000%) in the equilibrium constant would produce an error of only 22% in the calculated temperature. On the other hand, an error of as little as 50% in a K near 4 would produce an error of 22% in the calculated temperature. Furthermore, for a constant near 2, a 50% discrepancy in K would introduce an infinitely large error in T.

[5] Some conception of the degree of unreliability of this procedure may be obtained from the following information. The very precise data of Herbert C. Brown and his associates (1947) on certain gas-phase equilibria have been analyzed by a procedure essentially the same as that used by Brown and Patterson, in which entropies of reaction are neglected. Representative values of the temperatures calculated are: $-41{,}000$, $-4{,}500$, 2,500, 3,400, 4,500, and 7,100° K in all cases. The actual temperature at which the experiments were carried out was 373° K in all cases.

be maintained. The meager evidence which might be used for a qualitative estimate of the pressure points toward a much lower value. The figure of 1.5×10^5 atm quoted by Brown and Patterson is based on an assumed equilibrium temperature of 2,000° K. From the considerations outlined above, it is apparent that the temperature figure should be very much higher, and hence the pressure values considerably lower, perhaps even near 1 atm. There is certainly no convincing basis for a proposal of 10^5–10^6 atm. On the contrary, the evidence points toward pressures much too low to be "comparable to the internal pressures existing within Mars."

Thus, even if we grant (for the purposes of the present discussion) the questionable assumptions on the basis of which the computations have been made, we come to the conclusion that the more reliable of the data presented lead to temperatures far higher than the 3,000° reported by Brown and Patterson. Furthermore, their estimate of a pressure of 10^5–10^6 atm, calculated from an assumed temperature of 2,000° instead of 3,000°, cannot be maintained; for, as has been pointed out, the temperature calculations of greatest significance lead to values about five times higher than the assumed 2,000°; consequently, the pressures must be far below 10^5 atm, and a figure as low as 1 atm is entirely consistent with the available data.

Since the temperature and pressure values reported by Brown and Patterson are at variance with those obtained from a careful, critical analysis of the same basic data, any conclusions of cosmological significance drawn from their figures can hardly be proposed as compelling, let alone "irrefutable." While the hypothesis of a single planet of origin for meteorites may be an attractive one (*5*), as indeed its popularity for almost a century (*4*) testifies, there is as yet *no thermodynamic basis* for justifying this assumption.

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The Composition of Meteoritic Matter and the Origin of Meteorites

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Professor Klotz (*6*), in his interesting and vigorous discussion of the chemical interpretation by Patterson and the writer (*2*) of the composition of meteoritic matter, has undertaken an analysis of the possibilities of determining the temperatures within the planet from which meteorites may have had their origin. It is unfortunate that Professor Klotz' discussion evidences misinterpretation of the intent of our survey, of the methods used by us in arriving at our conclusions, of the validity of the data accumulated, and of the relative stress placed by us upon the various points in our argument. Each of these items deserves further comment.

In our investigations an effort was made primarily to see whether or not some sort of chemical order might exist in a field of inquiry where heretofore little order has been found. Our work was stimulated by the hope that, should indications of order become apparent, paths might be opened for fruitful and informative meteoritic research guided by sound chemical principles.

The sources of information utilized in our investigations of meteoritic relationships were varied, including notably:

(1) The variation of the nickel content in the metal phase of stony meteorites with the metal phase content and the relationships between the metal phase of stony meteorites and iron meteorites.

(2) The variation of the distribution coefficient of nickel between metal and silicate phases as a function of metal phase content.

(3) The dependence of the distribution coefficients of various elements between the silicate and metal phases upon the enthalpy change of the general reaction $M + FeSiO_3 \rightleftarrows MSiO_3 + Fe$ or $M + FeO \rightleftarrows MO + Fe$.

(4) The major differences existing between the me-