# Equilibrium at Low Pressure in the Reduction of Barium Oxide by Carbon

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## Equilibrium at Low Pressure in the Reduction of Barium Oxide by Carbon

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An experimental scheme to investigate the reduction equilibrium of barium oxide by carbon is described and analyzed critically. Exploratory results at 950° support the analysis and indicate equilibrium at carbon monoxide pressures below $100\mu$ with barium vapor pressures in the range 0.1 to $0.3\mu$. The resulting value for the free energy of formation of barium oxide is $-114,000$ cal. per mole.

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EVEN the most refractory oxides are reduced by carbon at low pressures and at temperatures sufficient to volatilize the reduced metal from the reaction zone. If metal vapor is kept in contact with an oxide-carbon mixture in a closed system, equilibrium should be attained. The reaction,

$$BaO(s) + C(s) = Ba(g) + CO(g),$$
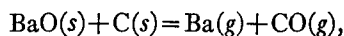
occurs readily in the activation of oxide coated cathodes. Use of a low pressure system to determine the equilibrium constant, $K = p_{CO} \cdot p_{Ba}$, poses substantial difficulties but results reported herewith indicate that it offers a most promising approach to the thermochemistry of barium oxide.

### EXPERIMENTAL METHOD

A barium oxide-powdered graphite mixture in a low ash graphite crucible was enclosed in a one-inch quartz tube (Fig. 1). The experimental scheme involves two constant temperature zones: a high temperature zone $T_2$ for the reaction mixture, and a lower temperature zone $T_1$ for a reservoir of solid barium. The pressure of barium vapor in contact with the reaction mixture is thereby maintained at a constant value determined by the vapor pressure of barium at $T_1$. Connection to a McLeod gauge through a capillary tube permits meas-

urement of the carbon monoxide pressure and limits the escape of barium vapor to avoid a pressure gradient between the $T_1$ and $T_2$ zones. The capillary tube simulates in effect a closed system with reaction mixture at $T_2$ and walls at $T_1$. In principle it can be made as small as desired. The 10-cm long, 2-mm diameter tube used constricts the escape of barium vapor to a value negligible compared with the capacity of the barium reservoir and permits easy evacuation or equalization of the carbon monoxide pressure between the McLeod gauge and the hot zones.

The pressure of carbon monoxide at equilibrium combined with the known pressure of barium vapor determines the equilibrium constant. Side reactions, such as reaction of barium vapor with the walls, and "gettering" of carbon monoxide by barium outside the $T_2$ zone, are to be expected. They need not influence the equilibrium pressures provided the equilibria of barium with its vapor at $T_1$ and of the reduction at $T_2$ adjust to pressure changes at a rate which is rapid compared with that of non-equilibrium processes. Evidence that this criterion for significant equilibrium results may be realized appears in the results.

The reaction mixture was formed from 200 mg of reagent grade barium carbonate mixed with an excess of powdered graphite. Barium was introduced in the form of nickel clad barium wire, the tube sealed off, evacuated, and heated to 1000° for one hour to convert carbonate to oxide and initiate reduction. The barium was then released from its nickel covering by heating with a high frequency induction coil. The temperature zones were maintained constant within 10° with resistance furnaces, and measured with calibrated chromel-alumel thermocouples.
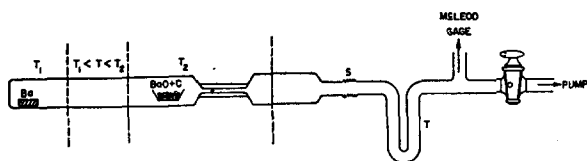
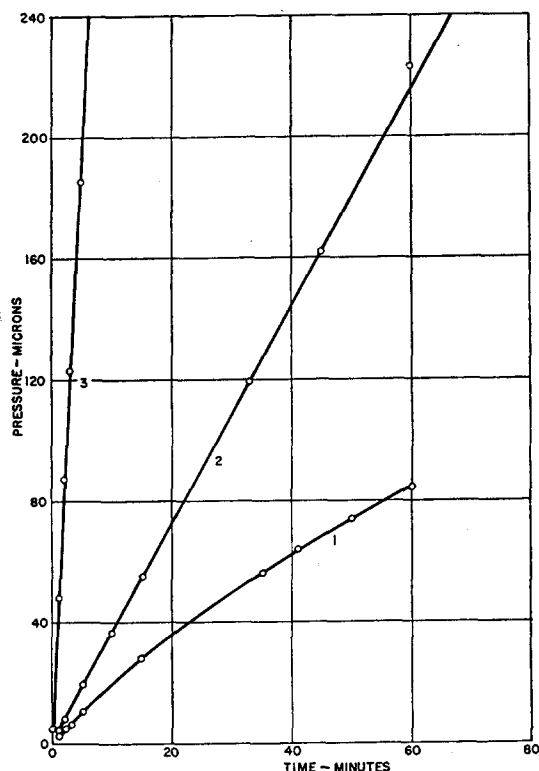

FIG. 1. Apparatus and method.

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FIG. 2. Rate of reaction. Curve 1—Graphite crucible alone. Curve 2—Graphite crucible+barium oxide. Curve 3—Graphite crucible+barium oxide-powdered graphite mixture.

## RESULTS

The normal progress of the reaction at 1000° with the $T_1$ zone cold appears in Fig. 2. The pressure increased linearly with time and fell off only moderately after repeated evacuations. The rate of reaction was highly dependent on the intimacy of contact. Gas evolution from the empty crucible, largely carbon monoxide without effect on the equilibrium, decreased considerably on repeated evacuation.

Evidence for equilibrium at 950° appears in Figs. 3 and 4. The initial point of each curve represents the time at which the evacuated system was closed off. The following rise in pressure, due to carbon monoxide, was markedly affected by the temperature $T_1$ of the barium reservoir, indicated at intervals along the curves. Increase of $T_1$ by 30° from 545° was calculated to increase the pressure of barium vapor from $0.10\mu$ to $0.25\mu$.[1] As the temperature $T_1$ was raised the pressure dropped abruptly from more than $60\mu$ to pressure plateaux at $29\mu$ and $25\mu$ in two tests. Possible complication from reaction of carbon monoxide with barium outside the $T_2$ zone is suggested by the anomalous drop in pressure (Fig. 3) which followed a drop in $T_1$ before the expected pressure rise. The somewhat lower pressure plateaux at $24\mu$ and $16\mu$ resulted when $T_1$ was held

constant at 570° rather than increased suddenly to that value after accumulation of excess carbon monoxide, so that equilibrium was approached from the reverse direction. The general consistency of the results is seen by comparison of the plateau at $69\pm4\mu$ for $T_1=545°$ ($p_{Ba}=0.10\mu$), followed for 50 minutes, with the average value of $25\mu$ at $T_1=575°$ ($p_{Ba}=0.25\mu$). Corresponding values of the equilibrium constant, $K=p_{Ba}\cdot p_{CO}$, are $11.9\times10^{-12}$ and $10.8\times10^{-12}$ sq. atmos. respectively. The free energy change in the reduction,

$$\Delta F^0=\Delta F_{BaO}{}^0-\Delta F_{CO}{}^0=-RT\ln K=-61,200\ \text{cal.}$$

When the well-established value for $\Delta F_{CO}{}^0=-52,600$ cal.[2] is substituted, a rounded value for the free energy of formation of barium oxide at 1223° abs. of $-114,000$ cal. is obtained.

### SIGNIFICANCE OF RESULTS

Establishment of the equilibrium constant within a factor of two corresponds to an uncertainty of $\pm1000$ cal. in the free energy of formation of barium oxide. The present exploratory results indicate an internal consistency at least within this accuracy although considerable further work is necessary to establish the absolute accuracy. Complications due to side reactions: mainly reaction of barium vapor with the quartz walls and reaction of barium with carbon monoxide outside the $T_2$ zone appear to be less serious than might be anticipated. It is suggested that these non-equilibrium
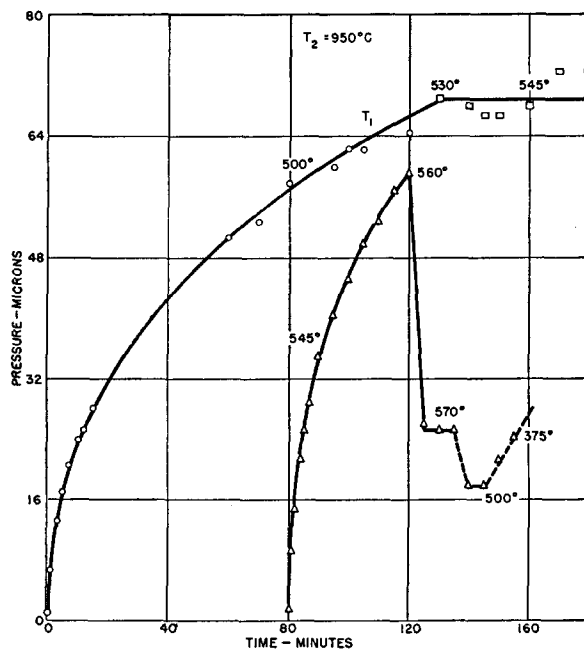


FIG. 3. Equilibrium at $p_{Ba}=0.10$ micron.

[1] Based on vapor pressure data for solid barium. E. Rudberg and J. Lempert, J. Chem. Phys. **3**, 627 (1935).

[2] Calculated at 1223° abs. from equation of M. deKay Thomson, "The Total and Free Energies of Formation of the Oxides of Thirty-Two Metals" (The Electrochemical Society, New York, 1942), p. 4.

processes decrease in rate as reaction proceeds and it is only necessary that the two equilibria:

$$Ba(s) = Ba(g) \text{ at } T_1 \qquad (1)$$

and

$$BaO(s) + C(s) = Ba(g) + CO(g) \text{ at } T_2, \qquad (2)$$
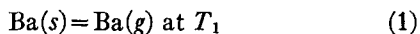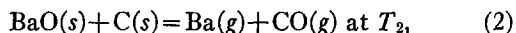
adjust with relative rapidity to pressure changes. A possible effect of thermal diffusion on the pressure of barium vapor at $T_2$ is inherent in the method, but its maximum value is given by the ratio $(T_2/T_1)^{\frac{1}{2}}$.

The possibility of solid solution of carbon in barium oxide, or the incidence of barium carbide formation, must also be considered. Equilibrium at 1141° and 1295°C in the formation of barium carbide from the oxide and carbon has been reported by M. deKay Thomson.[3] The reaction was considered to be

$$BaO + 3C = BaC_2 + CO. \qquad (3)$$
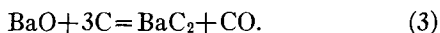
The equilibrium pressure of carbon monoxide was found to depend upon the composition of the solid mixture and it was concluded that a single solid solution of the three solids was necessary to account for the trivariance of the system. Thomson points out that dissociation of barium carbide into its elements occurs at higher temperatures, barium deposits on the walls, and the equilibrium measured is no longer that of reaction (3). The reaction,

$$2BaO + BaC_2 = 3Ba(g) + 2CO(g) \qquad (4)$$
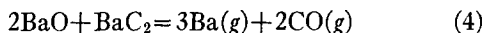
was not considered. Since carbon alone reduces barium oxide below 1000°C at low pressures, reduction by barium carbide by the reaction 4 is to be expected at much lower temperatures than dissociation of the carbide into its elements. The sum of reactions (3) and (4) gives the equilibrium (2) considered in the present work. Since our temperatures are considerably lower than those usually associated with barium carbide formation and the pressures are much lower than those used by Thomson, thereby favoring removal of any combined carbon by reaction (4), complication of the low pressure reduction by barium carbide is unlikely.

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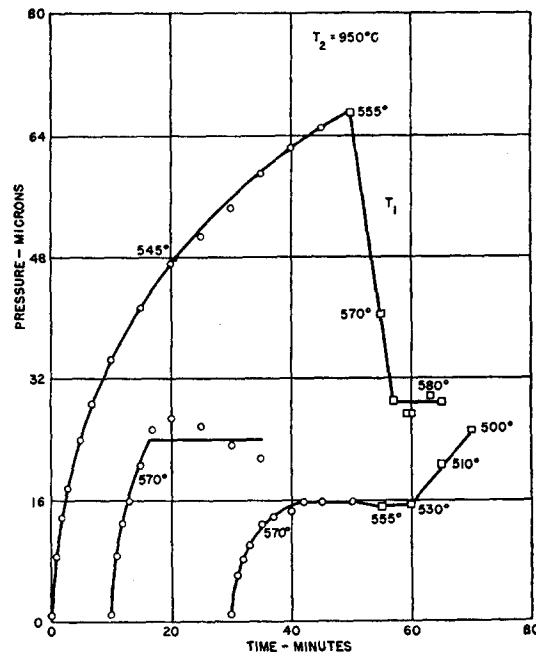[3] M. deKay Thomson, Trans. Am. Electrochem. Soc. 54, 91 (1928).



FIG. 4. Equilibrium at $p_{Ba} = 0.25$ microns.

The free energy of formation of barium oxide has been estimated by White[4] by application of the third law of thermodynamics to available specific heat data. Interpolation of his calculations gives a value of $-120,000$ cal. at 950°C, considered to be correct within 5000 cal. Recent determination of the high temperature specific heat of barium oxide[5] increases this estimate by about 1000 cal., and narrows the range of uncertainty in the third law value, now mainly in the heat of sublimation of metallic barium at room temperature. The present direct attack on the equilibrium constant thus indicates a value higher by a factor of ten than the third law value. For such a difficult system this is most encouraging agreement. With sufficient refinement and data at a series of temperatures, the equilibrium method should provide thermochemical constants of high accuracy.

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[4] A. H. White, J. App. Phys. 20, 856 (1949).
[5] J. J. Lander, private communication for early publication in J. Am. Chem. Soc.