

FEB 28 1967

MACD-JF 54-0108 '08

# GIBBS FREE ENERGY OF WATER AT ELEVATED TEMPERATURES AND PRESSURES WITH APPLICATIONS TO THE BRUCITE-PERICLASE EQUILIBRIUM<sup>1</sup>

GORDON J. F. MACDONALD<sup>2</sup>  
Cambridge, Massachusetts

## ABSTRACT

Tables of the Gibbs free energy of water for temperatures up to 800° C. and pressures up to 2,500 bars are presented. These tables have been prepared by using Keenan and Keyes's thermodynamic data on water at low pressures and by graphically integrating Kennedy's specific-volume data to high pressures. The equilibrium curve for the brucite-periclase reaction is calculated by using these data, and the results of the calculations are compared with direct experimental work on the system  $MgO-H_2O$ .

## INTRODUCTION

A great many of the reactions of interest to igneous, metamorphic, and sedimentary petrologists involve water as one of the major components. A knowledge of the thermochemical properties of water, coupled with the thermochemical properties of the solid phases involved in the reaction, allows the calculation of the equilibrium pressures and temperatures for the reaction. Such calculations provide an independent check on the equilibrium relations determined directly in hydrothermal experiments and allow predictions of equilibrium relations in systems not as yet studied experimentally. The water that takes part in such reactions in nature and in hydrothermal bombs is, in general, not pure  $H_2O$ . The water is probably saturated with the components of the solid phases with which it is in contact and, in nature, may form complex solutions with other gases, such as  $CO_2$ . The thermochemical properties of water in such complex solutions will, in general, differ from those of pure

water. However, calculations considering water as a pure component are in many cases useful approximations and serve as a starting point for a consideration of more complicated equilibria.

## AVAILABLE EXPERIMENTAL DATA

Keenan and Keyes (1936) present tables for the entropy and enthalpy of water up to 5,500 lbs/sq in (about 380 bars) and 1,600° F. (871° C.). These tables summarize the thermochemical data on water available up to 1936. Osborne, Stimson, and Ginning (1939) report thermochemical values for water along the saturation curve. In a recent study Keyes (1949) confirms the thermodynamic consistency of the data on water up to 550° C. and the accuracy of the Keenan and Keyes tables.

Kennedy (1950) determined the specific volume of water in the temperature range 200°–600° C. for pressures up to 2,500 bars. For the temperature range 600°–900° C. measurements were made for pressures ranging from 100 to 1,400 bars. Kennedy extrapolated his results in the 600°–900° C. temperature range to 2,500 bars pressure. This extrapolation is based on the constancy of  $(\partial P/\partial T)_V$  at high temperatures and pressures.

<sup>1</sup> Paper 137 published under the auspices of the Committee on Experimental Geology and Geophysics and the Division of Geological Sciences at Harvard University. Manuscript received June 7, 1954.

<sup>2</sup> Department of Geology and Geophysics, Massachusetts Institute of Technology.

## METHODS OF CALCULATION

Since much hydrothermal experimentation has been carried out at pressures higher than 5,500 lbs/sq in (380 bars) and since reactions of geological importance may take place at considerably higher water pressure, it is desirable to extend Keenan and Keyes's thermodynamic data to higher pressures by using Kennedy's (1950) measurements of specific volumes.

The Keenan and Keyes tables provide data for the entropy and enthalpy of water at a constant pressure over a range of temperatures. This information plus Kennedy's specific volume measurements can be combined to give thermochemical data in either of two ways. The first method, essentially that used by Keenan and Keyes in constructing their tables, is to use an integrated form of Maxwell's equations to determine the enthalpy and entropy of water at some pressure. These equations are

$$S = S_0 - \int_{P_0}^P \left( \frac{\partial V}{\partial T} \right)_P dP$$

and

$$H = H_0 + \int_{P_0}^P \left( \frac{\partial (V\tau)}{\partial \tau} \right)_P dP,$$

where  $S$  and  $H$  are the desired entropy and enthalpy,  $S_0$  and  $H_0$  are the entropy and enthalpy at the given starting pressure,  $V$  is the volume, and  $\tau$  is the reciprocal temperature. The derivatives  $(\partial V / \partial T)_P$  and  $[\partial (V\tau) / \partial \tau]_P$  can be evaluated from tabulated numerical values of the volumes either by direct numerical or graphical differentiation or by differentiation of an equation of state fitted to the volume data. Evaluating the derivatives from the table is unsatisfactory, in that it depends on the differentiation of experimental data. The tabulated volume data are affected in an unpredictable

way by rounding errors and random experimental errors. Differentiation tends to exaggerate such errors. These difficulties are not circumvented by first fitting an equation of state to the experimental data, particularly if the equation is one of many constants, since the equation will tend to reproduce the irregularities of the experimental data.

A second method of extending the available thermodynamic data is to calculate the Gibbs free energy directly from experimental data. The Gibbs free energy,  $G$ , of water at a series of temperatures at a constant pressure is determined from Keenan and Keyes's data by the relation  $G = H - TS$ . The variation of the free energy with pressure is given by

$$\left( \frac{\partial G}{\partial P} \right)_T = V,$$

and therefore

$$G = G_0 + \int_{P_0}^P V dP,$$

where  $G$  is the required free energy at a pressure  $P$  and  $G_0$  is the free energy at some pressure  $P_0$ . In practice,  $G_0$  is calculated from Keenan and Keyes's data. In this method the experimental values are integrated; rounding and nonsystematic experimental errors tend to be reduced, though, of course, systematic errors remain. The disadvantage of this procedure is that only values of the free energy are obtained. To obtain values of the enthalpy and entropy, the free energy must be differentiated with respect to temperature. For most geological purposes, however, the free energy is the thermochemical quantity of interest. Data on the free energy as a function of temperature and pressure of water and solid phases involved in a reaction determine the equilibrium pressures and temperatures for the reaction.

Holser (1954), in an independent investigation, has carried out an integration of Kennedy's data in order to obtain values of the fugacity of water at high temperatures and pressures. The values of fugacity can be used to obtain the values of the free energy of water. For most geologic purposes, however, it is convenient to deal directly with values of the free energy.

Table 1 lists values of the negative

TABLE 1  
GIBBS FREE ENERGY OF WATER IN  
CAL/MOLE

| T (° C.) | 100 Bars      | 200 Bars      |
|----------|---------------|---------------|
| 200..... | 76,977 ± 50   | 76,928 ± 50   |
| 225..... | 77,618 ± 50   | 77,567 ± 50   |
| 250..... | 78,284 ± 55   | 78,231 ± 55   |
| 275..... | 78,975 ± 60   | 78,919 ± 60   |
| 300..... | 79,690 ± 60   | 79,631 ± 60   |
| 325..... | 80,430 ± 65   | 80,369 ± 65   |
| 350..... | 81,195 ± 70   | 81,133 ± 70   |
| 400..... | 83,644 ± 130  | 82,940 ± 170  |
| 425..... | 84,701 ± 140  | 83,936 ± 190  |
| 450..... | 85,767 ± 150  | 84,941 ± 200  |
| 475..... | 86,841 ± 160  | 85,958 ± 220  |
| 500..... | 87,925 ± 180  | 86,991 ± 230  |
| 525..... | 89,022 ± 190  | 88,037 ± 250  |
| 550..... | 90,125 ± 200  | 89,095 ± 270  |
| 575..... | 91,233 ± 210  | 90,162 ± 280  |
| 600..... | 92,349 ± 220  | 91,239 ± 300  |
| 625..... | 93,476 ± 230  | 92,320 ± 310  |
| 650..... | 94,612 ± 240  | 93,407 ± 330  |
| 675..... | 95,755 ± 250  | 94,502 ± 350  |
| 700..... | 96,907 ± 270  | 95,607 ± 360  |
| 725..... | 98,063 ± 280  | 96,721 ± 380  |
| 750..... | 99,220 ± 290  | 97,842 ± 400  |
| 775..... | 100,380 ± 300 | 98,964 ± 410  |
| 800..... | 101,541 ± 310 | 100,088 ± 430 |

Gibbs free energy of 1 mole of water for temperatures ranging from 200° to 800° C. and for 100 and 200 bars. The value of the heat of formation of liquid water at 298°16 K. is taken to be  $-68.312 \pm 0.02$  kcal/mole (Wagman *et al.*, 1945). Kelley's (1950) recommended value for the entropy of water of  $16.75 \pm 0.03$  cal/deg mole is used. The entropy and enthalpy values of Keenan and Keyes (1936) and of Osborne, Stimson, and Ginning (1939) are used to evaluate the

change in free energy in going from liquid water at 25° C. and 1 bar pressure to water at the temperatures listed in table 1 and 100 bars pressure. Two sets of values for 200 bars pressure have been derived; one from Keenan and Keyes's data for 200 bars, and another from the foregoing data at 100 bars extended to 200 bars by graphically integrating Kennedy's (1950) volume data. These two sets are in agreement and have been combined in table 1.

Table 2 lists values for  $G(TP) - G(T \text{ 200 bars})$ , where  $G(TP)$  is the free energy of 1 mole of water at the given temperature and pressure and  $G(T \text{ 200 bars})$  is the free energy at the given temperature and 200 bars pressure. The values in table 2 correspond to the integrated term in the expression

$$G(TP) = G(T \text{ 200 bars}) + \int_{200}^P V dP.$$

Values for  $G(T \text{ 200 bars})$  are listed in table 1.

The values in table 2 are derived by graphical integration of Kennedy's (1950) data on the volume of water at elevated temperatures and pressures. In tables 1 and 2 no values are listed for 375° C. This is due to the large uncertainty in volumes and thermal data in the immediate region of the critical point.

#### ACCURACY OF FREE-ENERGY VALUES

Estimates of the uncertainties in the values of the free energy of water at 100 bars and 200 bars are listed in table 1. These estimates are based in part on Keyes's (1949) study of the consistency of water data, and Wagman *et al.*'s (1945) and Kelley's (1950) studies of liquid water. The estimate of the uncertainty of the values in table 2 is 4 per cent of the listed value. Kennedy's (1950) measurements on specific volume

TABLE 2  
VALUES FOR  $G(TP) - G(T \text{ 200 BARS})$  FOR WATER IN CAL/MOLE

| P<br>(BARR) | T (° C.) |       |       |       |       |       |       |       |       |       |       |       |       |
|-------------|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|             | 200      | 225   | 250   | 275   | 300   | 325   | 350   | 400   | 425   | 450   | 475   | 500   | 525   |
| 300....     | 49       | 51    | 52    | 55    | 58    | 64    | 69    | 250   | 336   | 401   | 450   | 488   | 521   |
| 400....     | 98       | 101   | 104   | 109   | 115   | 125   | 135   | 353   | 505   | 622   | 715   | 790   | 857   |
| 500....     | 146      | 151   | 155   | 162   | 170   | 184   | 198   | 431   | 606   | 751   | 876   | 987   | 1,085 |
| 600....     | 194      | 200   | 206   | 215   | 225   | 247   | 259   | 504   | 689   | 848   | 993   | 1,130 | 1,254 |
| 700....     | 241      | 249   | 256   | 267   | 279   | 299   | 319   | 574   | 762   | 933   | 1,093 | 1,246 | 1,390 |
| 800....     | 288      | 298   | 306   | 319   | 333   | 355   | 378   | 641   | 834   | 1,012 | 1,181 | 1,345 | 1,503 |
| 900....     | 335      | 346   | 356   | 371   | 386   | 411   | 436   | 705   | 903   | 1,087 | 1,263 | 1,435 | 1,603 |
| 1,000....   | 382      | 394   | 405   | 422   | 439   | 466   | 493   | 767   | 969   | 1,158 | 1,340 | 1,518 | 1,694 |
| 1,100....   | 428      | 442   | 454   | 473   | 491   | 520   | 549   | 828   | 1,033 | 1,227 | 1,414 | 1,598 | 1,779 |
| 1,200....   | 474      | 489   | 502   | 523   | 543   | 574   | 604   | 888   | 1,096 | 1,294 | 1,485 | 1,674 | 1,859 |
| 1,300....   | 520      | 536   | 550   | 573   | 594   | 627   | 659   | 948   | 1,158 | 1,359 | 1,553 | 1,746 | 1,936 |
| 1,400....   | 566      | 583   | 598   | 622   | 644   | 679   | 713   | 1,007 | 1,219 | 1,423 | 1,620 | 1,816 | 2,010 |
| 1,500....   | 612      | 630   | 646   | 671   | 694   | 731   | 767   | 1,065 | 1,279 | 1,485 | 1,685 | 1,884 | 2,082 |
| 1,600....   | 657      | 676   | 693   | 720   | 744   | 783   | 820   | 1,122 | 1,338 | 1,546 | 1,748 | 1,956 | 2,151 |
| 1,700....   | 702      | 722   | 740   | 768   | 794   | 834   | 873   | 1,178 | 1,396 | 1,606 | 1,810 | 2,015 | 2,219 |
| 1,800....   | 747      | 768   | 787   | 816   | 843   | 885   | 925   | 1,233 | 1,453 | 1,665 | 1,871 | 2,079 | 2,286 |
| 1,900....   | 791      | 813   | 833   | 864   | 892   | 935   | 977   | 1,288 | 1,510 | 1,724 | 1,932 | 2,142 | 2,352 |
| 2,000....   | 835      | 858   | 879   | 911   | 941   | 985   | 1,028 | 1,342 | 1,566 | 1,782 | 1,992 | 2,204 | 2,417 |
| 2,100....   | 879      | 903   | 925   | 958   | 989   | 1,034 | 1,079 | 1,396 | 1,622 | 1,839 | 2,052 | 2,265 | 2,481 |
| 2,200....   | 923      | 948   | 971   | 1,005 | 1,037 | 1,083 | 1,129 | 1,449 | 1,677 | 1,895 | 2,111 | 2,325 | 2,544 |
| 2,300....   | 967      | 993   | 1,017 | 1,051 | 1,085 | 1,132 | 1,179 | 1,501 | 1,731 | 1,951 | 2,169 | 2,385 | 2,606 |
| 2,400....   | 1,011    | 1,037 | 1,062 | 1,097 | 1,132 | 1,180 | 1,229 | 1,552 | 1,784 | 2,007 | 2,226 | 2,445 | 2,667 |
| 2,500....   | 1,054    | 1,081 | 1,107 | 1,143 | 1,179 | 1,228 | 1,279 | 1,603 | 1,837 | 2,062 | 2,283 | 2,505 | 2,728 |

TABLE 2—Continued

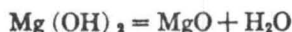
| P<br>(BARS) | T (°C.) |       |       |       |       |       |       |       |       |       |
|-------------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|             | 550     | 575   | 600   | 625   | 650   | 675   | 700   | 725   | 750   | 800   |
| 300....     | 556     | 587   | 620   | 649   | 676   | 703   | 732   | 757   | 780   | 824   |
| 400....     | 920     | 981   | 1,041 | 1,094 | 1,144 | 1,192 | 1,239 | 1,283 | 1,325 | 1,398 |
| 500....     | 1,177   | 1,263 | 1,345 | 1,419 | 1,488 | 1,553 | 1,616 | 1,676 | 1,733 | 1,836 |
| 600....     | 1,370   | 1,477 | 1,578 | 1,670 | 1,757 | 1,838 | 1,916 | 1,991 | 2,064 | 2,192 |
| 700....     | 1,525   | 1,649 | 1,766 | 1,875 | 1,978 | 2,074 | 2,165 | 2,251 | 2,337 | 2,491 |
| 800....     | 1,653   | 1,792 | 1,925 | 2,047 | 2,164 | 2,273 | 2,376 | 2,474 | 2,571 | 2,749 |
| 900....     | 1,765   | 1,917 | 2,062 | 2,196 | 2,324 | 2,444 | 2,559 | 2,668 | 2,777 | 2,973 |
| 1,000....   | 1,865   | 2,026 | 2,181 | 2,326 | 2,465 | 2,596 | 2,722 | 2,841 | 2,958 | 3,174 |
| 1,100....   | 1,957   | 2,126 | 2,290 | 2,444 | 2,592 | 2,733 | 2,868 | 2,996 | 3,125 | 3,356 |
| 1,200....   | 2,043   | 2,220 | 2,391 | 2,554 | 2,710 | 2,859 | 3,002 | 3,138 | 3,274 | 3,522 |
| 1,300....   | 2,125   | 2,308 | 2,486 | 2,656 | 2,819 | 2,976 | 3,126 | 3,269 | 3,412 | 3,675 |
| 1,400....   | 2,203   | 2,391 | 2,575 | 2,751 | 2,921 | 3,085 | 3,241 | 3,391 | 3,540 | 3,817 |
| 1,500....   | 2,279   | 2,471 | 2,660 | 2,841 | 3,017 | 3,187 | 3,349 | 3,505 | 3,660 | 3,950 |
| 1,600....   | 2,352   | 2,548 | 2,742 | 2,928 | 3,109 | 3,283 | 3,450 | 3,612 | 3,773 | 4,075 |
| 1,700....   | 2,423   | 2,622 | 2,821 | 3,012 | 3,197 | 3,375 | 3,547 | 3,714 | 3,880 | 4,194 |
| 1,800....   | 2,493   | 2,695 | 2,897 | 3,093 | 3,282 | 3,464 | 3,640 | 3,812 | 3,983 | 4,307 |
| 1,900....   | 2,562   | 2,767 | 2,971 | 3,171 | 3,364 | 3,550 | 3,730 | 3,906 | 4,081 | 4,414 |
| 2,000....   | 2,629   | 2,837 | 3,044 | 3,247 | 3,443 | 3,633 | 3,817 | 3,996 | 4,175 | 4,517 |
| 2,100....   | 2,695   | 2,905 | 3,116 | 3,321 | 3,520 | 3,713 | 3,901 | 4,083 | 4,266 | 4,616 |
| 2,200....   | 2,760   | 2,972 | 3,186 | 3,393 | 3,595 | 3,791 | 3,982 | 4,168 | 4,355 | 4,712 |
| 2,300....   | 2,824   | 3,038 | 3,255 | 3,464 | 3,668 | 3,867 | 4,061 | 4,251 | 4,441 | 4,805 |
| 2,400....   | 2,887   | 3,104 | 3,323 | 3,534 | 3,740 | 3,942 | 4,138 | 4,331 | 4,524 | 4,894 |
| 2,500....   | 2,950   | 3,169 | 3,390 | 3,603 | 3,811 | 4,015 | 4,213 | 4,409 | 4,605 | 4,982 |

of water strictly refer to water saturated with iron or iron oxide and other components of the bomb wall. These impurities in the water probably have a negligible effect on the measured specific volumes. The integration of the volumes to obtain the free-energy values tends to smooth out random experimental errors, though systematic errors in the volume determinations remain. A better estimate of the accuracy of Kennedy's data awaits further studies on water.

#### BRUCITE-PERICLASE EQUILIBRIUM RELATIONS

##### INTRODUCTION

A thermochemical study of the reaction



illustrates the use of the data presented in tables 1 and 2. Bowen and Tuttle (1949) and Roy, Roy, and Osborn (1953) determined experimentally equilibrium relations at elevated temperatures and pressures. The calculated equilibrium relation can thus be compared with the experimental determinations. Several thermochemical studies have been carried out on brucite and periclase, and reliable thermochemical values are available on these two phases.

##### THERMOCHEMICAL DATA

Heat-of-solution measurements on periclase and brucite have been carried out by Giauque and Archibald (1937), Taylor and Wells (1938), and Torgeson and Sahama (1948). Taylor and Wells found that the heat of reaction for



at 298°16 K. varied with the method of preparation of periclase and brucite. If MgO is prepared by dehydrating brucite for 2.5 hours at 450° C. and the  $\text{Mg}(\text{OH})_2$  used for the calculation is natural brucite,

the heat of this reaction is  $10.03 \pm 0.07$  kcal. Using MgO formed by dehydrating brucite at 1,425° C. for 2 hours and  $\text{Mg}(\text{OH})_2$  prepared by hydrating MgO at 177° C. in saturated steam for 2 hours, one obtains a heat of reaction of  $8.84 \pm 0.05$  kcal. The heat of reaction is  $9.79 \pm 0.07$  kcal for MgO prepared from brucite at 450° C., and synthetic brucite.

Taylor and Wells (1938) attribute the variation in heats of reaction to variations in the grain size of the brucite and periclase. Sedimentation experiments showed that MgO prepared at 800° C. contained abundant material less than  $1 \mu$  in size and considerable material less than  $0.5 \mu$ . MgO prepared at 1,315° C. had little material finer than  $1 \mu$ . X-ray examination did not reveal any phases other than periclase in the dehydrated  $\text{Mg}(\text{OH})_2$ . Dr. Hatten S. Yoder, Jr., in reviewing the manuscript, suggested that the variation in the measured heats of reaction may be due to incomplete conversion of  $\text{Mg}(\text{OH})_2$  and/or subsequent hydration of the MgO to  $\text{Mg}(\text{OH})_2$ . Such incomplete reaction or hydration might affect the heat-of-solution measurements in an irregular way; however, Taylor and Wells report consistent variations in heats-of-solution measurements for MgO prepared at temperatures ranging from 450° to 1,425° C.

Parks and Kelley (1926) determined the entropy of "coarse" crystalline periclase. They obtained a value of 6.4 cal/deg mole.\* Giauque and Archibald (1937) determined the entropy of finely powdered periclase and obtained a value of 6.66 cal/deg mole. Giauque and Archibald determined the entropy of brucite as  $15.09 \pm 0.05$  cal/deg mole.

Heat-capacity data for periclase are available over the entire temperature range of interest (Kelley, 1949). The

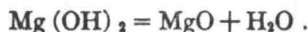
\* Originally reported as 6.6 cal/deg mole and later corrected (Kelley, 1950) to 6.4 cal/deg mole.

What is the heat of reaction for brucite?

heat-capacity equation recommended by Kelley (1949) is strictly valid only to 600° K. In the present calculation the equation has been used up to 900° K. The molar volume of periclase used in the calculation is  $11.23 \pm 0.09$  cc/mole, derived from X-ray measurements by Jay and Andrews (1946) and densities reviewed by Palache, Berman, and Frondel (1944). The molar volume of brucite used is  $24.31 \pm 0.1$  cc/mole. This value is based on X-ray and directly determined densities listed by Palache, Berman, and Frondel (1944). No corrections were applied to the volumes of brucite and periclase at high temperatures and pressures. The error due to neglect of volume corrections is small for pressures of 2,500 bars.

#### CALCULATED EQUILIBRIUM CURVES

Two equilibrium curves are calculated for the reaction



One curve is calculated by using the value of  $\Delta H$  for the reaction of  $10.03 \pm 0.15$  kcal/mole and the entropy of fine-grained periclase,  $6.66 \pm 0.1$  cal/deg mole. Thus this equilibrium curve corresponds strictly to equilibrium between periclase formed by dehydration of brucite at 450° C. for 2.5 hours and natural brucite. This equilibrium curve might be interpreted as corresponding to equilibrium between well-crystallized, coarse-grained brucite and poorly crystallized, fine-grained periclase. This curve is curve A in figure 1.

A second curve, curve B in figure 1, has been calculated on the basis of data for periclase formed by dehydration of brucite at high temperatures and synthetic brucite. This curve probably corresponds to equilibrium between fine-grained, poorly crystallized brucite and

coarse-grained, well-crystallized periclase.

Curve A lies about 60° higher than curve B. This is due to the higher free energy of periclase formed at 450° C. as

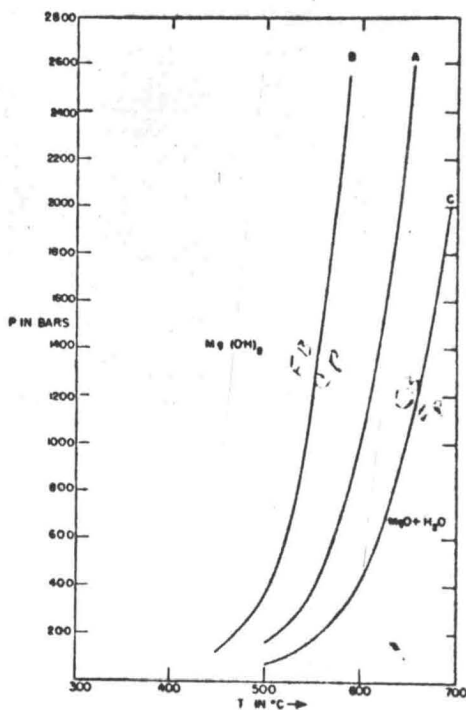


FIG. 1.—Equilibrium curves for reaction  $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$ . Curves A and B are calculated from thermochemical data. Curve A refers to equilibrium between natural brucite and periclase formed by the dehydration of brucite at low temperatures. Curve B refers to equilibrium between synthetic brucite and periclase formed by dehydration of brucite at elevated temperatures. Curve C was determined experimentally by Roy, Roy, and Osborn (1953). Pressure is the total water pressure acting on the system.

compared with that formed at 1,425° C. This higher free energy is probably largely the result of the higher surface area of the low-temperature periclase and correspondingly higher surface energy.

A set of curves between curves A and B could be drawn. These would correspond to equilibria between brucites and periclases in differing physical states. As discussed previously, the difference be-

tween curves *A* and *B* may be due in part to use of partially hydrated MgO in the heat-of-solution measurements.

Table 3 lists the equilibrium tempera-

TABLE 3  
EQUILIBRIUM TEMPERATURES AND  
PRESSURES FOR THE REACTION  
 $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$

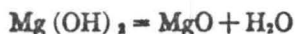
| Water Pressure<br>(Bars) | Equilibrium<br>Temperature<br>(° C.) |
|--------------------------|--------------------------------------|
| <i>Curve A:</i>          |                                      |
| 160.....                 | 500 ± 40                             |
| 370.....                 | 550 ± 45                             |
| 1,000.....               | 600 ± 50                             |
| 2,400.....               | 650 ± 60                             |
| <i>Curve B:</i>          |                                      |
| 130.....                 | 450 ± 35                             |
| 360.....                 | 500 ± 40                             |
| 650.....                 | 525 ± 45                             |
| 1,240.....               | 550 ± 50                             |
| 2,100.....               | 575 ± 60                             |

tures and water pressures for the brucite-periclase equilibria. The uncertainties in the temperatures correspond to the uncertainties in the thermal data, as discussed previously.

Curves *A* and *B* could be extended to lower temperatures by using Keenan and Keyes's (1936) data for water pressures lower than 100 bars. It is of interest to examine the course of curves *A* and *B* at very low water pressures. For temperatures on the order of 200°–300° C. and water pressures on the order of 1 atm., water vapor can be treated as an ideal gas. In this case the vapor pressure of water in equilibrium with brucite is given by the expression

$$P = e^{-\Delta G/RT},$$

where  $\Delta G$  refers to the change in free energy for the reaction



and where the reactants are in their standard state at the given temperature. Using this expression and the thermochemical data reviewed earlier, the low-

temperature extensions of curves *A* and *B* have been calculated and are presented in table 4.

Calculations based on the assumption that water acts as an ideal gas even at high pressures demonstrate the effect of the nonideality of water on the position of the equilibrium curve. Thus 520 bars of "ideal water" would be in equilibrium with brucite at 600° C., while 1,000 bars of real water are in equilibrium with brucite, according to the calculations leading to curve *A*. Other calculations assuming that water behaves like an ideal gas at high pressure would similarly be in error.

TABLE 4  
EQUILIBRIUM TEMPERATURES AND PRESSURES  
FOR THE REACTION  $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$ ,  
AT LOW VAPOR PRESSURES OF WATER

| Temperature<br>(° C.) | Equilibrium<br>Pressures for<br>Curve A<br>(Bars) | Equilibrium<br>Pressures for<br>Curve B<br>(Bars) |
|-----------------------|---------------------------------------------------|---------------------------------------------------|
| 25.....               | $9 \times 10^{-8}$                                | $6 \times 10^{-7}$                                |
| 127.....              | $6.2 \times 10^{-4}$                              | $2.4 \times 10^{-3}$                              |
| 190.....              | $2.2 \times 10^{-3}$                              | $6.5 \times 10^{-3}$                              |
| 212.....              | $5.6 \times 10^{-3}$                              | $1.7 \times 10^{-1}$                              |
| 327.....              | 3                                                 | 7.3                                               |

#### COMPARISON WITH EXPERIMENTAL RESULTS

Bowen and Tuttle (1949) present a breakdown curve for brucite, the breakdown taking place at about 890° C. at 400 bars water pressure, and extending nearly vertically to higher water pressures. Bowen and Tuttle's curve lies about 300° higher than curve *A* and is well outside the maximum limits of error in the calculated curve.

Roy, Roy, and Osborn (1953) present a detailed study of the brucite-periclase equilibrium. Their experimentally determined curve is curve *C* of figure 1. They used natural brucite, synthetic brucite, and C.P. MgO heated to 1,400° C. for

half an hour, as their starting materials. The principal difficulty encountered in the experimental study was the rapidity with which periclase hydrated to brucite. These authors considered that periclase was the stable phase whenever 20–30 per cent of the final material was periclase. In such cases the brucite present in the final product was considered to have formed by hydration of periclase at lower temperatures. They state that "the results using these criteria were reasonably consistent."

The results obtained, starting with natural brucite, can be compared with curve *A*, since the resulting periclase would probably be fine-grained and poorly crystallized. In addition, MgO is relatively insoluble in water at these temperatures and pressures, so that the dissolved materials in the water would have a relatively minor effect on the chemical potential of water. Starting materials other than natural brucite might result in equilibrium curves at lower temperatures, particularly if the experiments are not of long enough duration to allow recrystallization of the brucite or periclase. Apparently no such relations were observed in the experimental study.

Roy, Roy, and Osborn's curve lies at temperatures 50° higher than those of curve *A*, or just at the outer maximum limit of error of curve *A*. The discrepancy between the two curves might be explained by errors in the thermochemical data. There is the possibility that the error lies in fixing the criteria for equilibrium in the experimental study. That this might be so is suggested by the consistency of experimental results, despite the different starting materials.

#### GEOLOGICAL CONSIDERATIONS OF THE BRUCITE-PERICLASE EQUILIBRIUM

Neither brucite nor periclase may be considered common minerals. Brucite is

found in association with ultramafic rocks and in some cases in pseudomorphs after periclase. Brucite and periclase are found in dolomitic limestones that have been subjected to contact metamorphism. Tilley (1951) describes such periclase marbles from Skye. The periclase has rims of brucite, and there are brucite pseudomorphs after periclase. The periclase is thought to have resulted from the magnesian component of dolomite. Since periclase formed originally, rather than brucite, this association might be thought to give an indication of the water pressure and temperature during the metamorphism. Neither the calculated curve nor the experimental curve can be used in this regard. The solution in contact with the dolomite was probably a complex solution of water, carbon dioxide, and other components. The chemical potential of water in such a solution would be a sensitive function of the composition of the mixture. Different equilibrium curves would correspond to different compositions.

Curves *A*, *B*, and *C* all refer to equilibrium with the water pressure equal to the total pressure acting on the solid phases. If there is a high total pressure and low water pressure, the curves will be shifted to lower temperatures. Thus natural brucite and periclase prepared at 450° C. are in equilibrium at  $450^{\circ} \pm 50^{\circ}$  C. when the total pressure acting on the solid phases is 2,400 bars and the water pressure is 100 bars. If the water pressure were equal to the total pressure, then brucite and periclase would be in equilibrium at  $650^{\circ} \pm 60^{\circ}$  C. (curve *A*). Keeping the total pressure constant at 2,400 bars but lowering the water pressure from 2,400 bars to 100 bars decreases the equilibrium temperature from 650° to 450° C. The equilibrium curves that apply in nature will thus be a sensi-

tive function of the ratio of water pressure to rock pressure.

#### CONCLUSIONS

The availability of free-energy data on water over a wide temperature-pressure range should encourage the determination of the thermochemical properties of hydrous minerals. Heat of formation, entropy, and high-temperature heat-capacity data on hydrous minerals, together with the free-energy data presented here, would allow calculation of equilibrium curves involving these minerals. Such calculations not only would provide an independent test of present experimental work and a guide to future experimental

work but would also allow prediction of equilibrium relations in temperature-pressure regions difficultly accessible to direct investigation. In addition, high-temperature heat-capacity data alone on hydrous minerals might allow calculation of heat of formation and entropy of minerals from the experimentally determined equilibrium curves.

**ACKNOWLEDGMENTS.**—I wish to thank Professors Francis Birch and James B. Thompson, Hatten S. Yoder, Jr., Eugene C. Robertson, and Mr. E-an Zen for critically reviewing this manuscript and offering many helpful suggestions. I also wish to thank Professor George C. Kennedy for many stimulating discussions on the properties of water.

#### REFERENCES CITED

- BOWEN, N. L., and TUTTLE, O. F., 1949, The system  $\text{MgO-SiO}_2\text{-H}_2\text{O}$ : *Geol. Soc. America Bull.*, v. 60, p. 439-460.
- GIAUQUE, W. F., and ARCHIBALD, R. C., 1937, The entropy of water from third law of thermodynamics. The dissociation pressure and calorimetric heat of reaction  $\text{Mg(OH)}_2 = \text{MgO} + \text{H}_2\text{O}$ . The heat capacities of  $\text{Mg(OH)}_2$  and  $\text{MgO}$  from 20° to 300° K.: *Jour. Am. Chem. Soc.*, v. 59, p. 561-569.
- HOLSER, W. T., 1954, Fugacity of water at high temperatures and pressures: *Jour. Phys. Chemistry*, v. 58, p. 316-317.
- JAY, A. H., and ANDREWS, K. W., 1946, Note on oxide systems pertaining to steel-making furnace slags: *Jour. Iron-Steel Inst.*, v. 152, p. 15-18.
- KEENAN, J. H., and KEYES, F. G., 1936, Thermodynamic properties of steam: 89 p., New York, John Wiley & Sons, Inc.
- KELLEY, K. K., 1949, Contributions to the data on theoretical metallurgy. X. High temperature heat content, heat capacity and entropy data for inorganic compounds: *U.S. Bur. Mines Bull.* 476.
- 1950, Contributions to the data on theoretical metallurgy. XI. Entropies of inorganic substances, Revision (1948) of data and methods of calculation: *U.S. Bur. Mines Bull.* 477.
- KENNEDY, G. C., 1950, Pressure-volume-temperature relations in water at elevated temperatures and pressures: *Am. Jour. Sci.*, v. 252, p. 225-241.
- KEYES, F. G., 1949, The consistency of thermodynamic data for water substance vapor phase to 550° C.: *Jour. Chem. Physics*, v. 17, p. 923-934.
- OSBORNE, N. S., STIMSON, H. F., and GINNING, D. C., 1939, Thermal properties of saturated water and steam: *Jour. Research Natl. Bur. Standards*, v. 23, p. 261-270.
- PALACHE, C. BERMAN, H., and FRONDEL, C., 1944, *System of mineralogy*, v. 1, 7th ed.: 834 p., New York, John Wiley & Sons, Inc.
- PARKS, G. S., and KELLEY, K. K., 1926, The heat capacities of some metal oxides: *Jour. Phys. Chemistry*, v. 30, p. 47-55.
- ROY, D. M., ROY, R., and OSBORN, E., 1953, The system  $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$  and influence of carbonate and nitrate ions on the phase equilibria: *Am. Jour. Sci.*, v. 251, p. 337-361.
- TAYLOR, K., and WELLS, L., 1938, Studies of the heat of solution of calcium and magnesium oxides and hydroxides: *Jour. Research Natl. Bur. Standards*, v. 21, p. 133-149.
- TILLEY, C. E., 1951, The zone contact skarns of the Broadford area, Skye. A study of boron-fluorine metasomatism in dolomites: *Min. Mag.*, v. 24, p. 621-666.
- TORGESON, D. R., and SAHAMA, TH. G., 1948, A hydrofluoric acid solution calorimeter and the determination of heats of formation of  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$ , and  $\text{CaSiO}_3$ : *Jour. Am. Chem. Soc.*, v. 70, p. 2156-2160.
- WAGMAN, D. D., KILPATRICK, J. E., TAYLOR, W. J., PITZER, K. S., and ROSSINI, F. D., 1945, Heat, free energies and equilibrium constants of some reactions involving  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , C, CO,  $\text{CO}_2$ ,  $\text{CH}_4$ : *Jour. Research Natl. Bur. Standards*, v. 34, p. 143-161.