THE MAGNESIUM SULFATE-WATER SYSTEM AT PRESSURES TO 4 KILOBARS;

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Introduction. Hydrated magnesium sulfate constitutes up to one-sixth of the mass of carbonaceous chondrites, and probably is important in many icy asteroids and icy satellites. It occurs naturally in meteorites mostly as epsomite (the heptahydrate). $MgSO_4$, considered anhydrously, comprises nearly three-fourths of the highly soluble fraction of C1 chondrites [1]. Thus, $MgSO_4$ is probably an important solute in cryovolcanic brines erupted on certain icy objects in the outer solar system [2]. While the physicochemical properties of the water-magnesium sulfate system are well known at low pressures, planetological applications of these data are hindered by a dearth of useful published data at elevated pressures [but see 3]. Accordingly, we recently explored solid-liquid phase equilibria in this chemical system at pressures extending to about four kilobars.

Experimental. Except for improved insulation of the pressure vessel which reduced the rate of cooling and warming of the sample, the apparatus used was the same as described previously [4]. The 2.6 ml sample in the pressure vessel was pressurized by additional sample through small bore tubing extending from the cold bath to the pressure system. Mercury separated the sample from the pump fluid. Changes in sample volume produced corresponding changes in transducer voltage as a magnet floating on the mercury changed position.

Results. Figure 1 illustrates phase equilibria in the $MgSO_4$-H_2O system at 1 atm. A eutectic occurs near 17% $MgSO_4$ (by mass) where ice and magnesium sulfate dodecahydrate ($MgSO_4$.$12H_2O$) melt or freeze together at -3.9^0 C under equilibrium conditions. Table I gives approximate low-pressure densities of relevant phases and phase assemblages [5]. Polynomial fits were determined giving the density of 17 and 15.3 wt.% $MgSO_4$ solution as functions of temperature, T (in ^{0}C) at constant pressure, and pressure, P (in bars) at constant temperature. At approximately 50 bars, the lowest pressure investigated, the density of the 17% liquid is given (in g cm^{-3}) by the equation:

$$\rho = 1.19046 - (0.253577 \times 10^{-3}T) - (0.542964 \times 10^{-5} T^2) \tag{1}$$

Equation (1) is valid between $+5^0$C and -15^0C, and has a maximum deviation of 0.00006 g cm^{-3} over this range (we do not claim such good accuracy, which is on the order of 0.001 g cm^{-3}). The density of this 17% solution at 30^0C is given as a function of pressure by:

$$\rho = 1.17863 + (0.334949 \times 10^{-4} P) - (0.167615 \times 10^{-8} P^2) \tag{2}$$

Equation (2) is valid between 0 and 4000 bars, with a maximum deviation of 0.00082 g cm^{-3}. The density of 15.3% solution, at about 50 bars, is given by equation (3), valid from 24^0C to -16^0C.

$$\rho = 1.16985 - (0.250479 \times 10^{-3} T) - (0.253886 \times 10^{-5} T^2) \tag{3}$$

The maximum deviation of data from equation (3) is 0.00009 g cm^{-3}.
The density of 15.3% solution at 30^0C is given by equation (4), valid from 0 to 3950 bars.

$$\rho = 1.15756 + (0.339366 \times 10^{-4} P) - (0.179658 \times 10^{-8} P^2) \tag{4}$$

The maximum deviation from equation (4) is 0.0007 bars.
These data are consistent with published data [6,7] suitably extrapolated.

Figure 2 is a 2 kilobar run for 15.3 wt.% $MgSO_4$. The y-axis gives the measured voltage. The change in voltage is proportional to change in sample volume. The sample supercooled about 12K before crystallizing. The solution froze to a less dense assemblage (apparently ice I + $MgSO_4$.$12H_2O$) as seen by the increase in voltage (volume). The solid sample then locked up, thus preventing a volume change as indicated by the constant voltage as the sample cooled. Freezing was also accompanied by a 2 K temperature rise of the sample and bomb as heat was released during crystallization. The sample must have overpressurized during lock-up. The slow release of overpressurization is indicated as the sample slowly warmed through the subsolidus region and gradually expanded. At about 248.5 K the sample melted completely at the stable eutectic. The eutectic point was closely bracketed by two reversals, as shown by the thermal loops. The direct descent of the eutectic melting trajectory to the liquid cooling/warming curve indicates the absence of a liquidus solid phase above the eutectic temperature, further indicating that at 2000 bars the eutectic shifts to about 15.3% $MgSO_4$. This inference is supported by runs at 2000 bars and 17% $MgSO_4$ where excess magnesium sulfate melts on the liquidus above the eutectic temperature.

Figure 3 gives results for a run at 3460 bars, 17% $MgSO_4$. Crystallization was preceded by 18 K of supercooling; at this pressure the sample formed a denser assemblage of ice II + $MgSO_4$.$12H_2O$; the sample, as usual, locked after freezing. A temperature loop during the eutectic transition, requiring 4 hours to complete, bracketed the eutectic temperature at 3460 bars between 248.0 and 249.5 K, and confirmed that a dense solid liquidus phase (magnesium sulfate hydrate) melted at temperatures above the eutectic. Therefore, the eutectic composition at 3460 bars is still on the water-rich side of 17% $MgSO_4$.

The eutectic pressure-melting curve is shown in Figure 4. As expected for systems lacking significant solid solution, composition does not affect the eutectic temperature as long as the same solid assemblage is involved. The eutectic temperature at 50 bars, the lowest pressure we investigated, is consistent with the eutectic at 1-atm shown in Figure 1. The data below 2060 bars form a single smooth curve, strongly indicating no solid-state phase changes in $MgSO_4$.$12H_2O$ (and water ice) between pressures of 1 atm and 2060 bars. The melting curve has a slope break above 2060 bars, consistent with the ice I- ice II transition near this pressure. Another slope break is required near 3500 bars, consistent with the ice II - ice V transition. The relative magnitude of the volume changes at the eutectic melting transition are consistent with these various assemblages.

The data do not conclusively indicate whether or not $MgSO_4$.$12H_2O$ undergoes a solid-state phase change at pressures between 2 and 4 kilobars. Figure 4 implicitly assumes no such transition. A discrepant datum (with respect to Fig. 4) was obtained at 3 kilobars, where the melting transition occurred about 3.5 K higher than expected based on replicated data near 2 and 3.5 kilobars. This result is not understood since all the runs, including that at 3 kilobars, appeared to be good ones. Perhaps the pressure interval between 2 and 3.5 kilobars is more complex than assumed, conceivably involving a phase change in solid magnesium sulfate hydrate.

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Conclusions. The system H_2O-$MgSO_4$ in the region of the eutectic exhibits qualitatively constant behavior between pressures of 1 atm and 2 kilobars. The eutectic melting curve closely follows that for water ice, with a freezing point depression of about 4 K at 1 atm decreasing to around 3.3 K at 2 kilobars. The eutectic shifts from 17% $MgSO_4$ at 1 atm to about 15.3% $MgSO_4$ at 2 kilobars. Above 2 kilobars the eutectic melting curve again tends to follow that of ice, including changes in slope at pressures consistent with ice transitions, although the freezing point depression relative to the pure ice melting curve increases to 6 K at 4 kilobars.

References. 1. Fredriksson, K. and J.F. Kerridge, 1988, Meteoritics 23, 35-44. **2.** Kargel, J.S., 1991, (ABSTRACT) this volume. **3.** Livshits, L.D., et al., Russ. Jour. Inorg. Chem., 8, 676-678. **4.** Hogenboom, D.L., and J.S. Kargel, 1990, (ABSTRACT) Lun. Planet. Sci. XXI, 522-523. **5.** Kargel, J.S., 1990, Cryomagmatism in the Outer Solar System, Ph.D. dissertation, Univ. of Arizona, Tucson, 309 pp. **6.** Chen, C.T.A. et al., 1980, J. Chem. Eng. Data 25, 307-310. **7.** CRC Handbook of Chemistry and Physics.

TABLE I. Densities in $MgSO_4$-H_2O system

Phase(s)	Density (g cm^{-3}) @ 1 atm, 269 K
Water	1.000
Ice	0.917
$MgSO_4 \cdot 12H_2O$	1.47 +-0.06
Eutectic liquid	1.19
Frozen eutectic	1.12 +-0.02
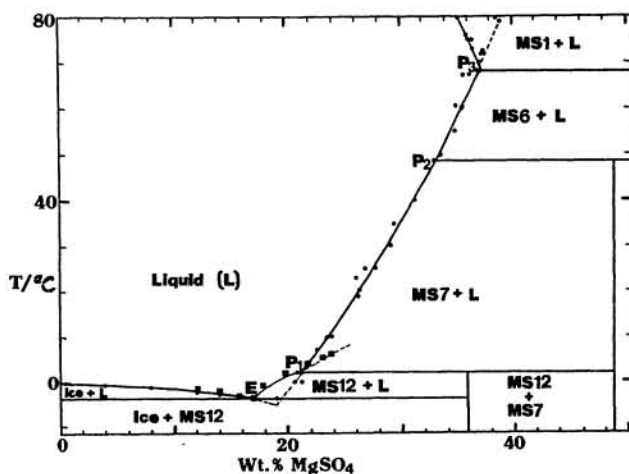
Figure 1. System H_2O-$MgSO_4$ at 1-atm.
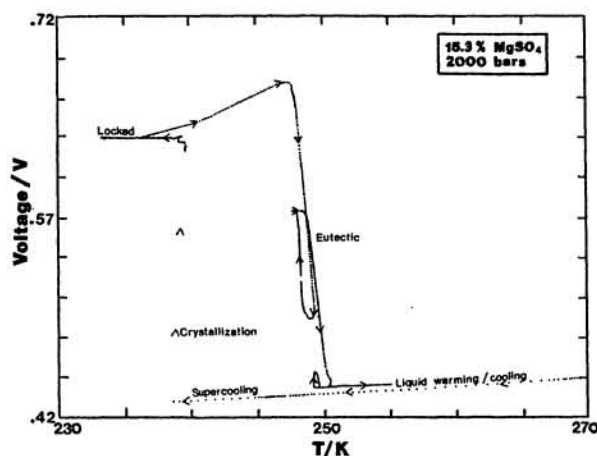
Figure 2. Run at 2000 bars for 15.3 wt.% $MgSO_4$.
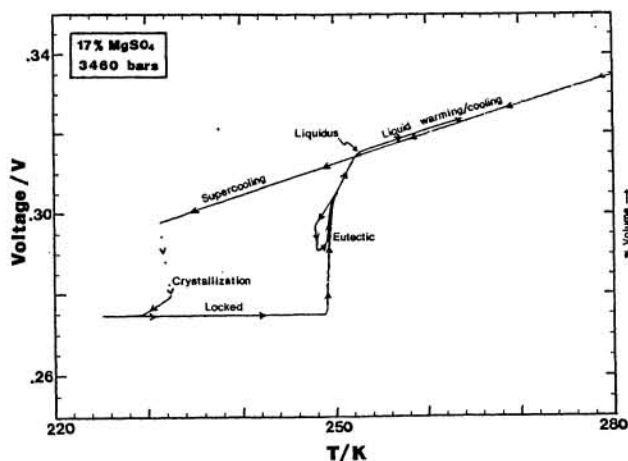
Figure 3. Run at 3460 bars for 17 wt.% $MgSO_4$.
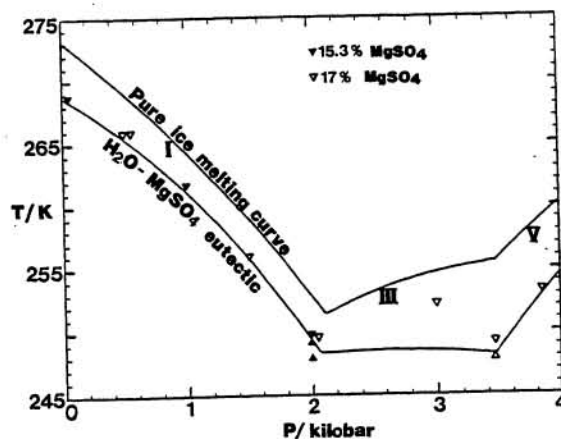
Figure 4. Melting curve for ice and H_2O-$MgSO_4$ eutectic.