Interfacial Tensions Between Molten Magnesium and Salts of the $MgCl_2$–KCl–$BaCl_2$ System

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Interfacial tensions between molten magnesium and salts of the $MgCl_2$–KCl–$BaCl_2$ system were determined by a maximum bubble pressure technique. The interfacial tensions vary from about 350–450 dyn/cm and are inversely proportional to temperature for the 675–900° C temperature range of measurement. At 800° C, $MgCl_2$ contents of 10–30 mol % give maximum interfacial tensions, while $MgCl_2$ contents of 80–90% give minimum.

This paper presents the data obtained under Part III of a program to determine the physical properties of molten salts pertinent to the magnesium industry. In particular, salts of the $MgCl_2$-KCl-$BaCl_2$ ternary system have been investigated. In the previous studies (*4*, *5*), densities and surface tensions of the salt system were determined as a function of composition and temperature. In this part of the program, the interfacial tensions between molten magnesium and various salts of the system were determined.

Interfacial tension is the driving force for coalescence of the magnesium and salt phases and is an important factor governing the ability of the salt phase to wet the magnesium phase. Harkins (*3*) has described the conditions for wetting or spreading of one liquid over another. Thus, in any particular environment, if the sum of the surface tension of the molten salt plus the magnesium-salt interfacial tension is less than the surface tension of the magnesium phase in that environment, the molten salt should wet the magnesium; the greater the difference, the greater should be the tendency for the salt to wet.

PROCEDURE

The magnesium-salt interfacial tensions were determined in a closed system under an argon atmosphere by a maximum bubble pressure technique. A head of molten magnesium and argon pressure were used to force magnesium bubbles from an orifice into the molten salt phase. From measurements of the net pressure required to form the bubbles, the magnesium-salt interfacial tensions were calculated using the equation of Schroedinger (*7*).

$$\gamma = \frac{PRg}{2}\left[1 - (2/3)(R/h) - (1/6)(R/h^2)\right] \qquad (1)$$

Schroedinger's equation is considered valid in the region where $(R/h)^{1/2}$ is less than 0.2. This condition was met in the experimental work. In the calculations, the last term of Equation 1 was insignificant and was neglected. The densities for the salt phases were taken from the data reported in the author's density paper (*4*). The density for magnesium was taken from unpublished work by the author which indicates that:

$$\rho_{Mg} = 1.562 - 2.6 \times 10^{-4}\,(T - 700°\,C);\ (t = 675\text{–}800°\,C) \qquad (2)$$

The technique required many mechanical manipulations and measurements to obtain the data. However, it was preferred over the sessile drop method because the determinations were made on continually generated interfaces and were, therefore, less likely to be affected by contamination. The bubble pressure method also did not depend on visual observation of the melt.

The equipment for making the measurements is illustrated in Figure 1. A 400 series stainless steel crucible positioned at the bottom of the shell held the salt charge. The magnesium charge was contained in the stainless steel "bubble tip holder". The capillary bore or bubble tip, made

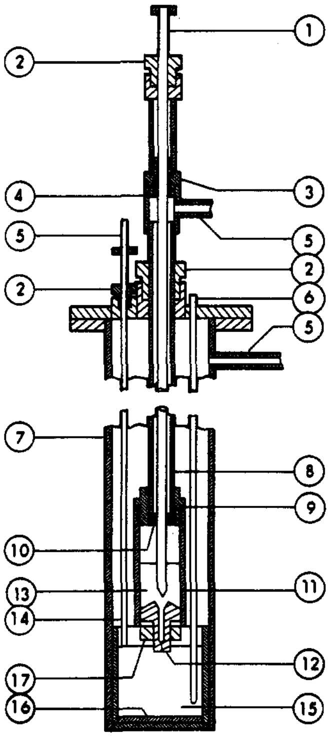

Figure 1. Schematic of interfacial tension apparatus

1. Electrical probe
2. Packing glands
3. Nylon insulator
4. Steel bushing
5. Argon inlets
6. Thermocouple well
7. Shell
8. Bubble tube
9. 300 S. S. gasket
10. Aluminum oxide insulator
11. Bubble tip holder
12. Bubble tip of Graph-I-Tite
13. Mg charge
14. Level tube
15. Salt charge
16. Crucible
17. Retainer nut of Graph-I-Tite

(Note: Unless otherwise stated, all material is 400 series stainless steel.)

Table I. Analysis of Mg-1 Used in Experiments

% Al	0.027	% Pb	>0.010
% Ca	>0.01	% Si	>0.01
% Cu	>0.001	% Sn	>0.01
% Fe	0.002	% Zn	>0.003
% Mn	0.004	% Zr	>0.01
% Ni	>0.001	% Be	>0.001

of Graph-I-Tite was attached to the bottom of the holder with a suitable nut of Graph-I-Tite. The bubble tip holder assembly entered the shell through a packing gland and could be moved in a vertical direction. Within the bubble tip holder assembly, there was an independently movable stainless steel rod that was sealed to the assembly and electrically insulated from it. This rod served the dual purpose of being an electrical probe to measure the level of magnesium in the bubble tip holder and a valve stem to shut off the flow of magnesium from the holder to the salt bath. The bubble tip holder assembly also had an argon gas inlet through which pressure was applied to form the magnesium bubble.

Outside of the bubble tip holder assembly and within the shell there was a thermocouple well and a movable level tube sealed to the shell flange by a packing gland. The level tube through which argon could be passed was used to measure the level of the salt bath in the crucible. The shell was also equipped with outlets so that the system could be evacuated, vented and broken to argon. The argon, which was purified by passing it through a bed of titanium sponge maintained at 760° C, could be independently fed to the shell, the bubble tip holder assembly and the level tube.

One arm of a manometer, not shown in the sketch, could be opened by suitable valving to either the bubble tip holder or the level tube. The other arm was open to the atmosphere. The manometer fluid was di-*n*-butyl phthalate which has a density of 1.040 g/cc at 25° C and a relatively low vapor pressure. Power to the resistance wound tube furnace was controlled manually with a variable inductor. Temperatures were determined potentiometrically with a chromel-alumel thermocouple. The level of the fluid in the manometer and the relative positions of the bubble tip holder assembly, the electrical probe and the level tube were determined with a cathetometer which could be read to 0.005 cm.

Considerable preparation and preliminary measurements had to be taken before the start of each experiment. The nominal diameter of the bubble tip bore ranged from 0.7–1.0 mm. The tips, if not new were pickled in HCl, rinsed in water, and dried prior to a run. The face of the clean tip was polished on 4/0 paper and the bore reamed with a tapered wood toothpick until the surface of the tip was

Table II. Example of: Surface Tension Data for $MgCl_2$–KCl–$BaCl_2$ Mixtures

($MgCl_2$–KCl System)

Salt system	Mol %			Temp, ° C	γ, dyn/cm
	$MgCl_2$	KCl	$BaCl_2$		
KCl + $MgCl_2$	10.0	90.0	. . .	798	412, 407, 410, 400
				725	437, 438, 423, 430, 420, 421
				775	414, 417, 417, 421, 417, 417
				820	404, 397, 409, 403, 412
	20.0	80.0	. . .	823	436, 429, 431, 424, 426, 429
				703	447, 455, 457, 458, 458, 457
				744	436, 436, 444, 447, 451, 438
	35.0	65.0	. . .	802	450, 445, 452, 435, 435, 434
				699	455, 455, 455, 455, 450
				723	448, 451, 445, 445, 443, 455
	50.0	50.0	. . .	703	456, 449, 460, 452
				799	426, 434, 432, 435, 448, 439
				752	442, 446, 433, 422, 425
				849	399, 400, 404, 394
	75.0	25.0	. . .	807	389, 388, 388, 377, 383, 384
				677	418, 418, 417, 415, 414, 414
				723	401, 404, 402, 401, 398, 402
				780	385, 383, 386, 387, 384, 385
	75.0	25.0	. . .	800	376, 376, 379, 374, 375, 376
				823	380, 375, 368, 374, 368
				701	417, 407, 407, 412, 412, 410
				677	418, 420, 418, 421, 418, 423
				723	410, 407, 410, 407, 404, 402
				775	390, 386, 384
KCl + $MgCl_2$	90.0	10.0	. . .	802	364, 366, 365, 364, 365, 364
				699	390, 389, 392, 390, 392, 392
				721	384, 384, 383, 382, 382, 381
				778	368, 368, 368, 364, 366, 366
	90.0	10.0	. . .	826	355, 348, 348, 352, 350, 349
				719	380, 380, 382, 382, 379, 380
				781	362, 362, 358, 360, 362, 362
				741	374, 375, 372, 370
	100	. . .	. . .	803	369, 369, 372, 369, 370, 369
				727	398, 394, 392, 391, 387, 391
				780	375, 376, 372, 373, 374, 376
				828	359, 362, 364, 361, 360, 361
	100	. . .	. . .	824	360, 364, 362, 360, 363, 359
				728	398, 400, 398, 400, 400, 398
				779	392, 383, 383, 380, 371, 376

perpendicular to the bore and the edge of the bore was reasonably uniform, circular, and sharp. The diameter of the finished bore was measured on a calibrated microscope to 2.5×10^{-3} mm. The tips were rotated on the microscope table and sixteen different measurements of the diameter were made with the average taken to be the diameter of the bore. Attempts were made to use other metals such as titanium, molybdenum, and 400 series stainless steel as tip materials to achieve a bore having a sharper edge than that obtainable with the Graph-I-Tite but none of them were satisfactory. The metal tips would be preferentially wetted by the salt phase at the beginning of an experiment but as the run progressed they became preferentially wetted in some areas by the magnesium. This changed the diameter of the bubble being formed and caused erroneous results.

The lengths of the assembled bubble tip holder and level tube relative to a scribe mark on each of the units as well as the distance of the electrical probe when seated in the Graph-I-Tite bubble tip to the face of the bore were determined prior to a run by suitable means to 0.001 in. (0.025 mm). With these measurements, it was possible to know the relative position of the units in the assembled system and to determine the depth of the molten phases within and outside the bubble tip holder and above the face of the bore.

The magnesium charge consisted of machined cylinders of Mg-1 that were about 3.8 cm. in diameter by 2.5 cm. long. Mg-1 analysis is presented in Table I. The machined pieces were wire brushed, pickled in 20% chromic acid cleaning solution, rinsed, and dried before placing them in the bubble tip holder. The salts used in the experiments were the same as described in previous papers (*4*, *5*), and were dried in the same manner. Likewise, the salt mixes were formulated by adding the ingredients to the crucible in their proper proportions. No attempt was made to check the composition of the melt after a run.

The thoroughly cleaned equipment was assembled with the salt charge in the crucible, the magnesium in the bubble tip holder and the level tube and bubble tip holder in the cooler section of the shell. The system was evacuated and dried under vacuum with the salt charge at 300° C for at least 10 hr. Then the system was broken to argon and the temperature of the salt charge brought up to 50–100° C above the melting point of the salt or magnesium. Once at temperature, the system was vented to the atmosphere and continually flushed with argon. It was not possible to operate with the system closed to the

Table III. Mg-Salt Interfacial Tensions and Corresponding Temperature Coefficients of $MgCl_2$–KCl–$BaCl_2$ Mixtures at 800° C

$$\gamma_t = \gamma_{800} - K[t - 800° C]$$

Salt system	Mol %					
	$MgCl_2$	KCl	$BaCl_2$	γ_{800} dyn/cm[a]	K, dyn/cm/° C[b]	Temp range of measurements, ° C
KCl + $MgCl_2$	10.0	90.0	. . .	409 ± 3	0.25	725–820
	20.0	80.0	. . .	433 ± 3	0.21	703–823
	35.0	65.0	. . .	442 ± 3	0.11	698–802
	50.0	50.0	. . .	424 ± 5	0.32	703–849
	75.0	25.0	. . .	383 ± 2	0.25	677–807
	75.0	25.0	. . .	379 ± 2	0.34	677–830
	90.0	10.0	. . .	363 ± 1	0.26	699–802
	90.0	10.0	. . .	357 ± 1	0.28	719–826
	100.0	. . .	. . .	370 ± 1	0.30	727–829
	100.0	. . .	. . .	371 ± 3	0.39	728–824
$BaCl_2$ + $MgCl_2$	40.0	. . .	60.0	407[c] ± 4	0.30	816–916
	60.0	. . .	40.0	389 ± 2	0.24	676–799
	80.0	. . .	20.0	369 ± 2	0.31	681–813
90% KCl–10% $BaCl_2$ + $MgCl_2$	25.0	67.5	7.5	425 ± 2	0.17	677–803
	40.0	54.0	6.0	427 ± 1	0.24	676–800
	60.0	36.0	4.0	412 ± 5	0.17	678–803
	80.0	18.0	2.0	384 ± 1	0.26	682–804
80% KCl–20% $BaCl_2$ + $MgCl_2$	15.0	68.0	17.0	431 ± 3	0.25	677–801
	30.0	56.0	14.0	418 ± 2	0.24	671–797
	50.0	40.0	10.0	399 ± 1	0.25	675–799
	70.0	24.0	6.0	368 ± 1	0.24	681–801
	85.0	12.0	3.0	359 ± 1	0.25	675–802
65% KCl–35% $BaCl_2$ + $MgCl_2$	10.0	58.5	31.5	416 ± 3	0.17	673–799
	20.0	52.0	28.0	416 ± 2	0.24	677–799
	40.0	39.0	21.0	408 ± 3	0.26	676–800
	60.0	26.0	14.0	367 ± 1	0.25	676–800
	80.0	13.0	7.0	363 [illegible] 2	0.26	673–801
40% KCl–60% $BaCl_2$ + $MgCl_2$	15.0	34.0	51.0	416 ± 2	0.18	748–853
	30.0	28.0	42.0	418 ± 5	0.35	672–802
	50.0	20.0	30.0	361 ± 2	0.23	677–799
	50.0	20.0	30.0	369 ± 2	0.24	679–792
	70.0	12.0	18.0	393 ± 2	0.37	673–802
	70.0	12.0	18.0	368 ± 1	0.21	681–802
	90.0	4.0	6.0	357 ± 1	0.28	695–800
25% KCl–75% $BaCl_2$ + $MgCl_2$	15.0	21.3	63.7	485[c] ± 2	0.27	825–926
	30.0	17.5	52.5	403[c] ± 4	0.16	727–836
	45.0	13.8	41.2	390 ± 2	0.32	673–798
	60.0	10.0	30.0	403 ± 3	0.29	665–799
	60.0	10.0	30.0	366 ± 1	0.30	668–800
	80.0	5.0	15.0	373 ± 2	0.33	689–803

[a] γ_{800} is the value of the interfacial tension at 800° C according to the least-square line representing the change of interfacial tension with temperature for each system. The limits indicate the range within which the mean interfacial tension measurement at 800° C will reside at a 95% confidence level. [b] Range of the slope of the least-square line at a 95% confidence level. [c] Extrapolated.

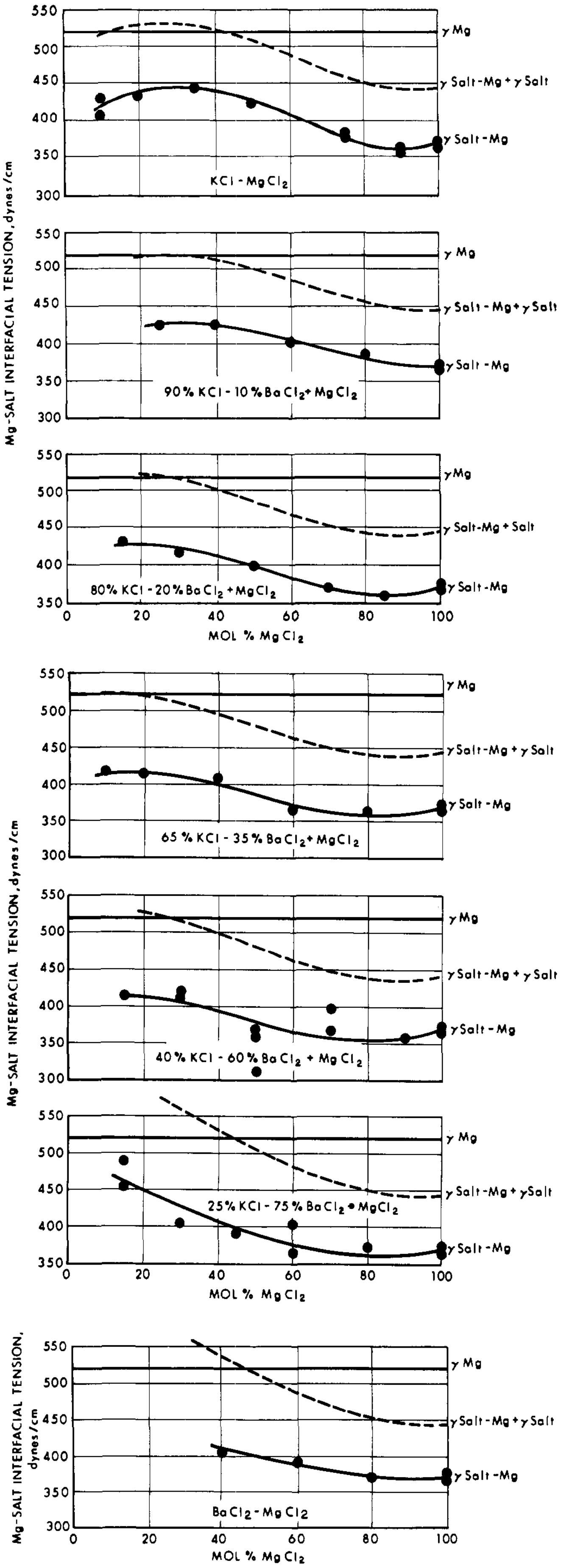

Figure 2. Mg-salt interfacial tension vs. $MgCl_2$ concentration at 800° C

atmosphere because of erratic fluctuations in pressure within the shell. Argon was passed through the level tube and bubble tip holder to keep them free of solids.

When the temperature of the salt melt was maintained constant within $\pm 2°$ C for 15 min, the level tube was lowered to locate the surface of the melt. Then the bubble tip holder was lowered so that the face of the tip was 0.635 cm beneath the melt surface. The argon to the bubble tip was vented so that the magnesium would not be forced out through the bore prematurely as it melted. When the magnesium was melted, its depth within the bubble tip holder was determined with the electrical probe.

Because of the small density differences between the molten salt and magnesium, a considerable amount of magnesium was needed to form an unstable bubble which would naturally break away from the tip. To conserve on magnesium—prior to forming a magnesium bubble—the electrical probe was threaded down until it was just short of seating so that, as soon as the maximum pressure was obtained, it could be used as a valve to shut off the magnesium flow from the bubble tip. Suitable corrections then had to be made for the height of the magnesium displaced by the immersed portion of the probe.

With the electrical probe in the near closed position, argon was slowly introduced into the bubble tip assembly and the pressure rise was noted by following the level change of the manometer fluid with the cathetometer until there was a sudden fall in pressure indicating the collapse of the bubble. After each bubble, the levels of salt and magnesium were redetermined. If magnesium was less dense than the salt being studied, the change in level of the salt was attributed to magnesium but, otherwise, it was considered as a change in salt depth. The position of the bubble tip was never changed from its first location and its depth of immersion was determined for each bubble from its relative location with the level tube.

After the above measurements were made, the procedure for generating the magnesium bubble was repeated until at least six reasonably consistent readings were obtained in succession. Then the salt temperature was brought to the next desired value and the series of measurements repeated. The temperature was normally raised in increments of 25–50° C until the maximum desired value was reached, then lowered in similar increments to the minimum value and then back up to near the original temperature. Using this technique, it was possible to determine if the data were consistent and if there had been any attack of the bore or change in composition of the melt through vaporization or hydrolysis during the run.

To determine if the bubbles were actually generated at the bore (tip preferentially wetted by the salt), or at the outside circumference of the tip (tip preferentially wetted by magnesium), measurements were made on the same magnesium-salt system under the same conditions, using tips of different dimensions. Tips with the same bore diameter but different outside diameters, and vice versa were evaluated. The results obtained by basing the calculations on the bore diameters rather than the tip diameters were consistent.

RESULTS

The magnesium-salt interfacial tensions were determined as a function of temperature and $MgCl_2$ content for the KCl-$MgCl_2$ and $BaCl_2$-$MgCl_2$ binaries, and for five psuedobinaries in which the ratio of KCl to $BaCl_2$ was maintained constant. It was not possible to obtain the data for the KCl-$BaCl_2$ system. With no $MgCl_2$ originally present in the salt, the tips made out of Graph-I-Tite were always attacked. It is believed that magnesium reacted with KCl to form $MgCl_2$ and potassium, and that the latter attacked the Graph-I-Tite.

For each particular salt mix, the magnesium-salt interfacial tensions were determined at a number of temperatures at approximately 25° C intervals over a temperature range of up to 125° C. The data collected are presented in Table II (*6*). When plots were made of interfacial tension vs. temperature for all salt compositions studied, the most consistent "best fit" was a straight line (with negative slope) over the temperature range studied. The appropriate lines, therefore, were determined by computer using a least-squares analysis. From each line, the 800° C interfacial tension value was determined along with the slope ($d\gamma/dt$). The results are presented in Table III. The limits associated with each interfacial tension define the statistical range of values within which the mean interfacial tension at 800° C will reside at a 95% confidence level. Duplicate runs on the same salt system are reported as such, rather than averaging them.

From the data in Table III, the change in magnesium-salt interfacial tension for each binary or pseudobinary at 800° C with $MgCl_2$ content is plotted (solid curves) in Figure 2. The dashed curves in Figure 2 represent the sum of the magnesium-salt interfacial tension and the surface tension of the salt in argon as determined earlier (*5*). The solid horizontal line at 529 dyn/cm is the surface tension of magnesium at 800° C according to Girov (*2*). The difference between it and the dashed curve represents the tendency for the particular salt system to wet magnesium. The iso-magnesium-salt interfacial tension curves for the ternary salt system at 800° C are presented in Figure 3. The contour lines representing the difference between the surface tension of magnesium, the sum of the magnesium-salt interfacial tension, and the surface tension of the salt are presented in Figure 4.

In general, the magnesium-salt interfacial tensions appear to go through a maximum with $MgCl_2$ content at 10–30% $MgCl_2$ and a minimum at 80–90% $MgCl_2$. As the ratio of KCl to $BaCl_2$ is reduced, the inflections become less pronounced. Wetting of magnesium is apparently favored by $MgCl_2$ contents greater than 30%; the lower the KCl-$BaCl_2$ ratio, the more $MgCl_2$ required to obtain wetting.

DISCUSSION

Probably the greatest source of experimental error in the procedure was the measurement of the diameter of the bubble tip bore. Though considerable care was taken in polishing and reaming the bore, it was not possible to obtain as sharp an edge as desired. As a result, it is possible that the measured diameter of the bore was less than the "effective" diameter and that this difference changed from run to run. This could explain the differences seen between some experiments made with the same salt mixture.

In spite of the difficulties of making the measurements, the results are reasonably consistent, not only for a particular binary system but from system to system. These results indicate that the magnesium-salt interfacial tensions go through a maximum with $MgCl_2$ contents of 10–30% $MgCl_2$ and a minimum at 80–90% $MgCl_2$. Wetting of the magnesium by the salt phase is promoted by $MgCl_2$ contents greater than 30% and the lower the KCl-$BaCl_2$ ratio, the more $MgCl_2$ is required to obtain wetting. Though it might be misleading to compare these results obtained under argon with performance of the salts as protective agents for molten magnesium in air, they are in general agreement. Better protection is usually provided by fluxes high in $MgCl_2$ content and low in $BaCl_2$.

It is interesting to compare the magnesium-salt interfacial tension results with the previously reported density and surface tension results. In the density work it was found that the molar volume curves for the KCl-$MgCl_2$ system exhibited relatively large positive deviations from ideal behavior within the 0 to 60% $MgCl_2$ concentration range and small negative deviations from about 60–100% $MgCl_2$. The positive deviation could be attributed to a high degree of covalent bonding and possibly to the existence of complexes (*1*). The effect of increasing the $BaCl_2$-KCl ratio in the density program was that of making the changes caused by the addition of $MgCl_2$ less pronounced. The general shape of the magnesium-salt interfacial tension curves are similar to the molar volume curves. Thus, it appears that an increase in the extent of covalent bonding of the $MgCl_2$ increases the magnesium-salt interfacial tension and lessens the ability of the salt to wet or protect magnesium. In general, the surface tension in argon curves were of opposite shape indicating that, as covalent bonding becomes more prevalent, relatively little energy is required to generate additional surface area.

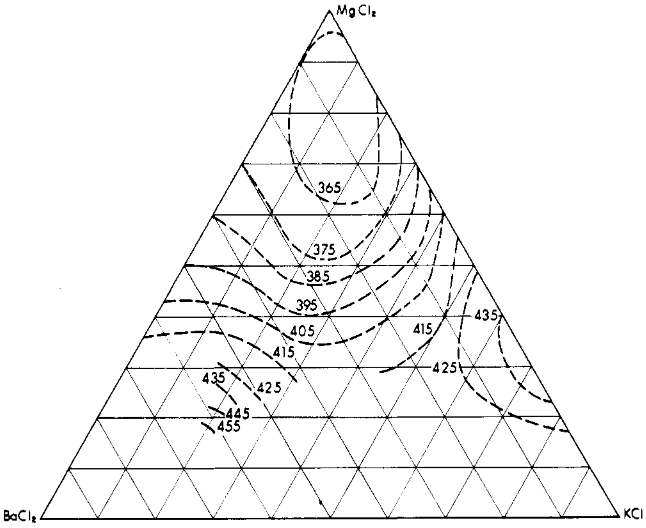

Figure 3. Iso-Mg-salt interfacial tensions for $MgCl_2$–KCl–$BaCl_2$ system at 800° C

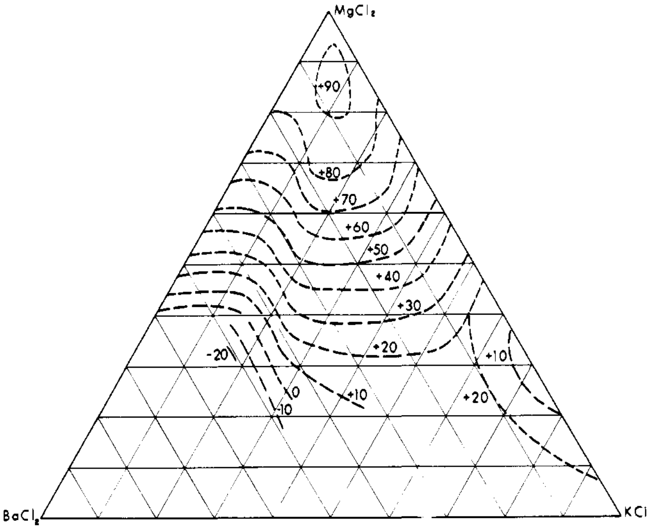

Figure 4. Contour curves representing: $\gamma_{Mg} - (\gamma_{Mg\text{-}salt} + \text{salt})$ at 800° C

ACKNOWLEDGMENT

The author gratefully acknowledges the help of R. O. Bolenbaugh who performed most of the experiments and collected the data reported in this paper.

NOMENCLATURE

$\bar{P}$ = the net pressure drop across the magnesium-salt interface and was assumed equal to the total pressure applied to the magnesium phase (sum of the gas pressure and hydrostatic pressure due to the magnesium head) minus the hydrostatic pressure of the salt phase at the bore tip, grams/cm^2

R = radius of the bore, cm

g = gravity, cm/sec^2

h = $\bar{P}/(\rho_s - \rho_{Mg})$, cm

Greek Letters

γ = the magnesium-salt interfacial tension, dyn/cm

ρ_s = density of the salt phase, grams/cm^3

ρ_{Mg} = density of the molten magnesium, grams per cm^3

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Low-Temperature Heat Capacity and Entropy of Ammonium Tetrametaphosphate

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The low-temperature heat capacity of ammonium tetrametaphosphate, $(NH_4PO_3)_4$, was measured over the temperature range 10–300° K. The heat capacity, C_p; entropy, $S°$; and Gibbs function, $(G° - H_0°)/T$, at 298.15° K are 110.23, 111.14, and -51.97 cal deg^{-1} mole^{-1}, respectively. The small upward shift in heat capacity over the range 200–300° K that occurred during the course of the measurements is thought to be the result of an unidentified monotropic transition of the material.

In a continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of ammonium tetrametaphosphate $(NH_4PO_3)_4$, was measured over the temperature range 10-300° K by adiabatic calorimetry.

Ammonium tetrametaphosphate is of interest in fertilizer technology because it has a moderately higher nutrient content than ammonium polyphosphates. In greenhouse tests, granular ammonium tetrametaphosphate produced significantly higher yields of maize forage than an equivalent amount of concentrated superphosphate. The degradation of tetrametaphosphate to orthophosphate in soils has not been described, but the results of the greenhouse test indicate that the cyclic form and its intermediate degradation products may be more effective sources of phosphorus than the usual orthophosphates.

MATERIALS AND APPARATUS

The calorimeter charge of ammonium tetrametaphosphate was prepared by metathesis of copper tetrametaphosphate and ammonium sulfide. The copper tetrametaphosphate was prepared by the method of Thilo and Rätz (*7*).

$$2CuO + 4H_3PO_4 = Cu_2(PO_3)_4 + 6H_2O \qquad (1)$$

Copper oxide (160 grams) was mixed with reagent phosphoric acid (246 ml, 85% H_3PO_4) to form a blue paste. The mixture was heated in a silica dish at 400° C for 8 hr to produce a light green solid, $Cu_2(PO_3)_4$.

The copper tetrametaphosphate was converted to ammonium tetrametaphosphate by the method of Warschauer (*10*). The copper salt (360 grams) was crushed, washed with water, and added in small portions to 810 ml of a stirred, cooled 20% $(NH_4)_2S$ solution to effect the metathesis

$$Cu_2(PO_3)_4 + 2(NH_4)_2S = (NH_4PO_3)_4 + 2CuS \qquad (2)$$

The precipitated copper sulfide was filtered off and the ammonium tetrametaphosphate (182 grams) was crystallized by addition of alcohol to the solution.

Recrystallization of the crude (95%) ammonium tetrametaphosphate at room temperature by adding methanol to its aqueous solution increased its purity only slightly; of its phosphate, 1% was present as ortho-, 1% as pyro-, and 2% as tripolyphosphate. Chromatographic analysis of the mother liquor showed that there had been considerable hydrolysis of the tetrametaphosphate; the phosphate was distributed as tetrameta- 73%, ortho- 2%, pyro- 5%, tripoly- 16%, tetrapoly- 3%, and more highly condensed phosphates 2%.

The recrystallization was repeated at 0° C to minimize hydrolysis. The crude $(NH_4PO_3)_4$ (152 grams) was dissolved in 220 ml of water at 0° C, the pH was adjusted to 7.0

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