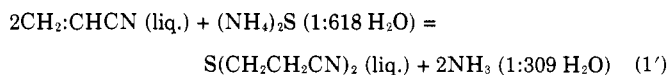


over the same temperature ranges. The heat of reaction was then evaluated by an enthalpy balance equation.

Results. For the reaction represented by the following equation:



the heat of reaction was determined as

$$\Delta H_{\text{rxn}} (25^\circ \text{C.}, 1 \text{ atm.}) = -30.20 \pm 0.6 \text{ kcal. per gram-mole TDPN.}$$

Since the $(\text{NH}_4)_2\text{S}$ and NH_3 solutions were sufficiently dilute, their standard heats of formation were taken as -55.21 and -19.27 kcal. per gram-mole (8), respectively. A value of $+36.20$ kcal. per gram-mole (1) was used for the standard heat of formation of $\text{CH}_2:\text{CHCN} (\text{liq.})$. Thus, the heat of formation of TDPN at 25°C. and 1 atm. is:

$$-30.20 - 2(-19.27) + 2(36.20) + (-55.21) = +25.53 \text{ kcal. per gram-mole.}$$

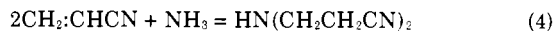
DISCUSSION

Acrylonitrile reacts readily with hydrogen sulfide in the presence of a basic catalyst to form TDPN according to the following equation (7):



The reaction in the calorimetric study with 0.2% ammonia catalyst was found to go practically to completion in 10 to 15 minutes.

Acrylonitrile may also react with ammonia or water according to the following equations (2, 4-6):



Under the conditions investigated, the above reactions were unimportant.

As a check on the chemical part of the thermochemical investigation, the organic layer in the calorimeter was separated and stripped of the more volatile substances by heating on a water bath and bubbling air through it. The final product was analyzed by gas chromatography and also by a method similar to that suggested by Witschonke (9). The purity of the TDPN product seemed not to deviate appreciably from that of the original charge. The result showed that the reaction which actually occurred in the calorimeter was primarily that represented by Equation 1. The side reactions in Equations 3, 4, 5, and 6 could have occurred, if at all, only to a very slight extent so that they could be tolerated without significant error.

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Surface Tensions and Corresponding Temperature Coefficients of Molten Magnesium Chloride, Potassium Chloride, and Barium Chloride Mixtures

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The results obtained from surface tension measurements of molten mixtures of MgCl_2 , KCl , and BaCl_2 by the maximum bubble pressure method are presented. The surface tensions at 800°C. and the corresponding temperature coefficients, as determined by interpolation of the plotted data, are presented for each composition studied.

THIS PAPER presents the data obtained under Part II of a program to determine the physical properties of molten salts pertinent to the magnesium industry. The surface tensions of the MgCl_2 - KCl - BaCl_2 ternary system as a function of composition and temperature were determined by the maximum bubble pressure method. The results obtained are presented in tabular and plot form for a series of binary systems. In each binary system, the ratio of barium chloride to potassium chloride is maintained constant while the ratio of the two salts to magnesium chloride is varied. The data obtained by other investigators for the binaries, KCl - MgCl_2 , BaCl_2 - MgCl_2 , and KCl - BaCl_2 , are also presented for comparison.

PROCEDURE

The surface tensions of the molten salts were determined by the maximum bubble pressure method using two tips of different diameters immersed in the melt to the same depth. Most investigators have used the single tip method (1-3). The double tip method was preferred for this work because it eliminated the need for accurate information on the depth of immersion of the tips. The double tip method is discussed by Harkins (4). Because of the hygroscopic nature of magnesium chloride, the surface tension measurements were made under an atmosphere of dry argon which was further purified by passage through a bed of titanium

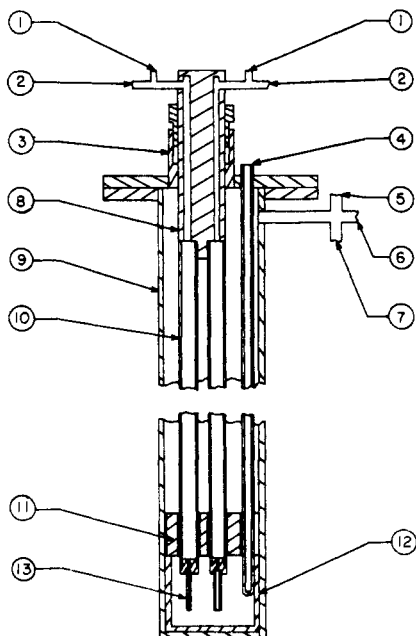


Figure 1. Schematic of surface tension apparatus

- 1-Connections to manometer; 2-Argon inlet to bubble tips; 3-Packing gland; 4-S.S. thermocouple well; 5-Argon inlet; 6-Vent; 7-Vacuum line; 8-Tube holder; 9-S.S. Shell; 10-Bubble tubes; 11-Crucible cover; 12-Graphite crucible; 13-Platinum bubble tips

sponge at 760°C. The major details of the apparatus are shown in Figure 1.

Each of the platinum—10% rhodium alloy bubble tips had its own argon supply and was individually connected to the manometer so that argon could be continually flowing through one tip while the gas pressure in the other tip was being measured. The manometer fluid was di-*n*-butyl phthalate.

The apparatus was positioned so that the crucible was within the uniform temperature region of a resistance-wound tube furnace. Temperatures were measured potentiometrically with a chromelalumel thermocouple having a cold junction. During each measurement, the temperature was controlled manually with a variable inductor.

The nominal bore diameters of the two tips were 76 and 2.5 mm. Various designs of bubble tips were evaluated to determine their sensitivity to depth of immersion and bubble rate. Bubble tips with a flat end and wide shoulder were less sensitive to these changes than tips with a very narrow shoulder or tips that came to a point. The effect of bubble rate on the results was determined in molten KCl. Care was taken to measure accurately the depth of immersion of the tips so that they could be considered separately as well as in combination with each other. These experiments indicated that the results varied with bubble rate and that the large bore was more sensitive to flow changes. The decision was made to operate at a flow rate of one bubble per 10 seconds since it resulted in good agreement among all three values.

Prior to a run, the tips were pickled in concentrated HCl, rinsed in water and alcohol, and dried. They were then placed in a special holder so that the end of the tips could be polished and the bore reamed with a jeweler's broach until the surface of the tip was perpendicular to the bore, and the edge of the bore was uniform, circular, and sharp. The diameter of the bores was measured with a calibrated microscope to 5×10^{-4} mm. on the small bore and 1.3×10^{-3} mm. on the large bore. The tips in their holders were

rotated on the microscope table, and 16 different measurements of the diameters were made. The average of the 16 measurements was taken to be the diameter of the bore. The tip assembly was also checked for length on a lathe. The tips were required to be within 0.05 mm. of each other. The above procedure was repeated before each run.

The salts used in these experiments were the same as described earlier (5), and they 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 author's procedure for operating the equipment was as follows: The thoroughly cleaned equipment was assembled with the charge and evacuated. The unit was dried under vacuum at 300°C. for at least 3 hours. Then the system was converted to argon and the temperature of the charge brought to 900°C. When the desired temperature was reached, the system was vented to the atmosphere and continually flushed with argon. A small flow of argon was also passed through the tips.

The tips were lowered until they contacted the surface which was noted by observing a pressure rise in the manometer. The tips were then lowered to within 15 mm. of the bottom of the crucible, and the melt was stirred by the bubbles for at least 15 minutes. Then the tips were raised to a level about 6 mm. below the originally measured melt surface. With the tips in position, the flow rates were adjusted by needle valves to rates of one bubble per 10 seconds. Before any pressure readings were taken, the temperature of the melt was maintained constant within $\pm 2^\circ\text{C}$. for 15 minutes. The maximum pressure data were taken by following the rise or fall of the fluid in the legs of the manometer with a cathetometer. Six readings were taken of each leg, averaged, and then subtracted from each other to determine the maximum gas pressure to the bubble tip. This was done for each bore. The cathetometer could be read to 0.005 cm., and the gas pressure readings ranged from 2.5 to 9.0 cm. of manometer fluid.

After the readings at 900°C. were taken, the temperature was normally raised to 925°C. and then dropped in steps of about 50°C. until 750°C. was reached. Then the temperature was increased in steps of 50°C. until the temperature

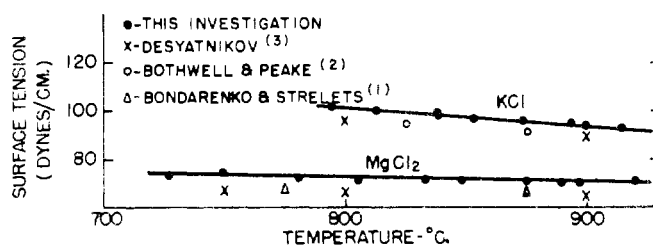


Figure 2. Surface tension of MgCl_2 and KCl vs. temperature

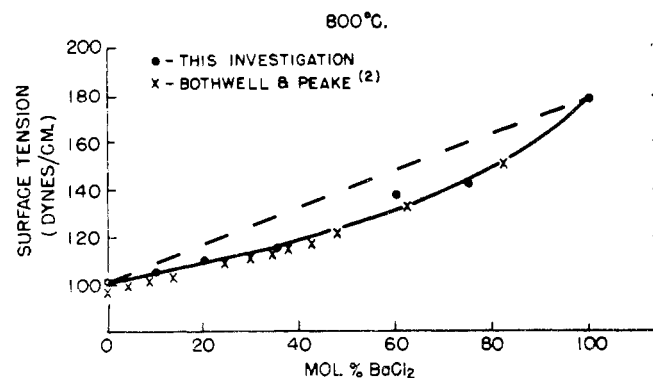


Figure 3. Surface tension of KCl— BaCl_2

was again at 900° C. In general, eight to nine determinations at different temperatures were taken over a 7-hour period with the same melt. By using this technique, it was possible to determine whether the results were consistent and whether there had been any attack of the bores or change in composition of the melt during the run.

To calculate the surface tension values from the data, it was assumed that the surface tension could be adequately determined with the data from each tip by the well-known equation:

$$\gamma = \frac{\bar{P}Rg}{2} \left[1 - \frac{2}{3} \left(\frac{R}{h} \right) \right] \quad (1)$$

Assuming that the tips are at the same depth, the following relationship is true:

$$\gamma = g/2[\Delta P_T] \left[\frac{R_1 R_2}{R_1 - R_2} \right] + \frac{1}{3} \rho [R_1 R_2] g \quad (2)$$

- γ = the surface tension of the melt, dynes/cm.
- \bar{P} = total gas pressure, P_T , applied to the tip less the hydrostatic pressure of the melt at the capillary tip, grams/cm².
- R = radius of the bore, cm.
- $h = (\bar{P}/\rho)$ where ρ is the density of the melt, cm.
- g = gravity, cm./sec².
- ΔP_T = the difference in total gas pressure applied to the two tips

Table I. Surface Tensions and Corresponding Temperature Coefficients of MgCl₂-KCl-BaCl₂ Mixtures at 800° C.

$$\gamma_t = \gamma_{800} + K [t - 800^\circ \text{C.}]$$

Mole %			γ , Dynes/ Cm.	$-K$, Dynes/ Cm./° C.
MgCl ₂	KCl	BaCl ₂		
...	100.0	...	101.1	0.074
10.0	90.0	...	86.3	0.058
10.0	90.0	...	95.7	0.066
20.8	79.2	...	87.6	0.074
35.0	65.0	...	83.1	0.060
50.0	50.0	...	79.9	0.050
75.0	25.0	...	78.8	0.047
90.0	10.0	...	78.3	0.031
100.0	71.8	0.016
...	...	100.0 ^a	177.7 ^b	0.078
25.0	...	75.0	142.4	0.070
40.0	...	60.0	120.2	0.041
60.0	...	40.0	100.2	0.040
80.0	...	20.0	83.8	0.035
...	90.0	10.0	105.0	0.084
10.0	81.0	9.0	98.4	0.074
25.0	67.5	7.5	88.9	0.057
40.0	54.0	6.0	86.2	0.060
60.0	36.0	4.0	80.3	0.046
80.0	18.0	2.0	77.3	0.043
...	80.0	20.0	109.5	0.074
15.0	68.0	17.0	97.0	0.063
30.0	56.0	14.0	88.6	0.061
50.0	40.0	10.0	83.6	0.062
70.0	24.0	6.0	80.9	0.056
85.0	12.0	3.0	75.8	0.048
...	65.0	35.0	114.4	0.069
10.0	58.5	31.5	105.5	0.067
20.0	52.0	28.0	98.9	0.065
40.0	39.0	21.0	90.1	0.066
60.0	26.0	14.0	89.3	0.051
80.0	13.0	7.0	81.3	0.035
...	40.0	60.0	138.3	0.081
15.0	34.0	51.0	118.1	0.044
30.0	28.0	42.0	106.6	0.061
50.0	20.0	30.0	100.2	0.044
70.0	12.0	18.0	87.9	0.033
90.0	4.0	6.0	77.0	0.019
...	25.0	75.0	142.4 ^b	0.055
15.0	21.2	63.8	139.3 ^b	0.059
15.0	21.2	63.8	131.8 ^b	0.060
30.0	17.5	52.5	121.6	0.060
45.0	13.8	41.2	119.0	0.055
60.0	10.0	30.0	99.6	0.046
80.0	5.0	15.0	85.9	0.023

^a Data for BaCl₂ from Bothwell and Peake.

^b Extrapolated values.

The reported results were calculated on the basis of Equation 2, after making proper corrections for thermal expansion of the bores. The densities used in the calculations were taken from the data reported in the author's density paper.

EXPERIMENTAL RESULTS

The experimental results of this investigation are presented in Table I. Figure 2 is a plot of the experimental data

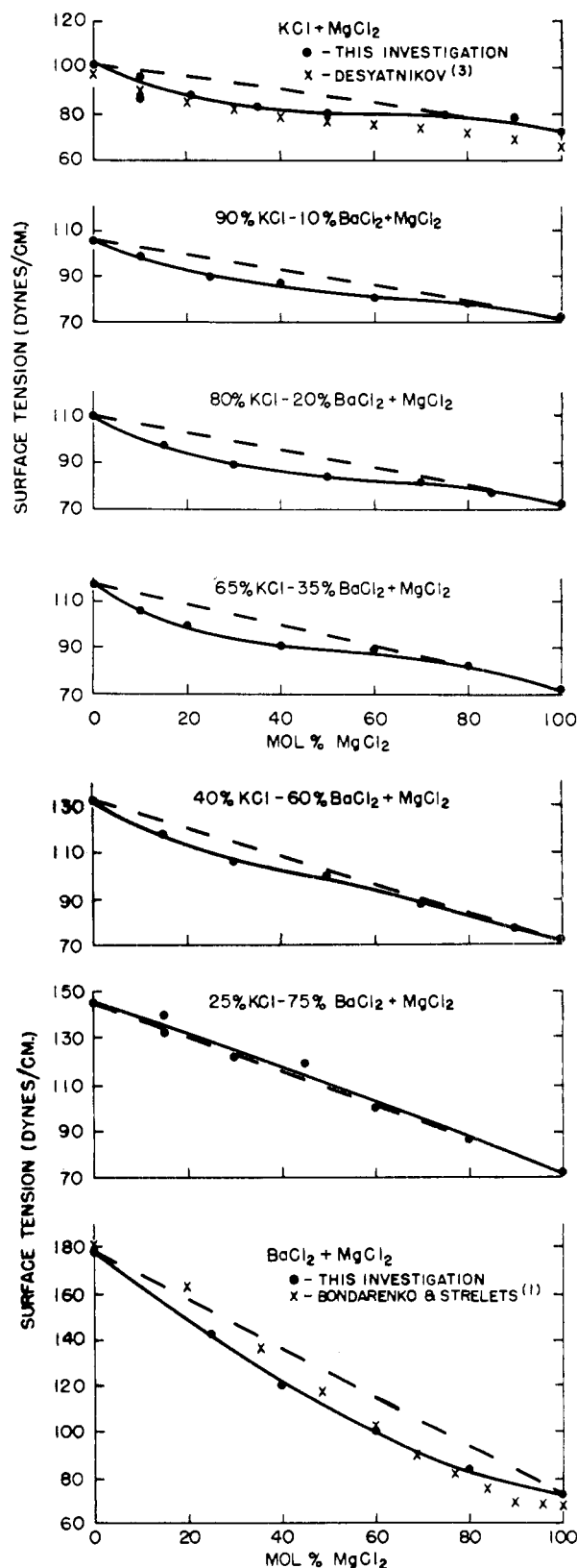


Figure 4. Surface tension vs. MgCl₂ concentration at 800° C.

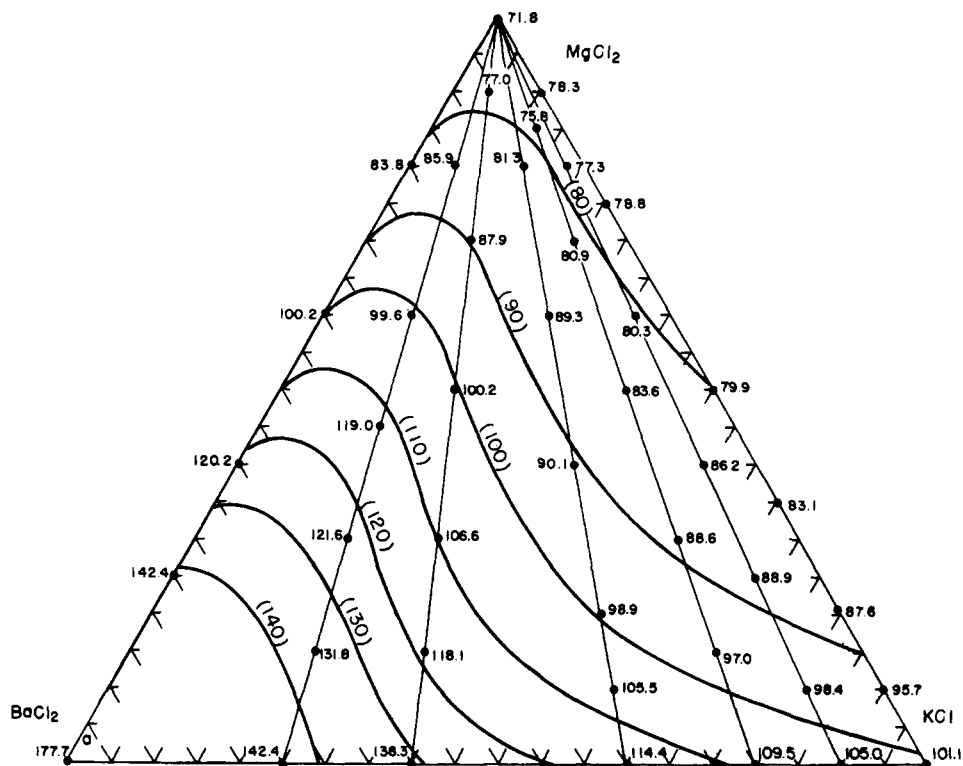


Figure 5. Surface tension of $\text{MgCl}_2\text{-KCl-BaCl}_2$ system
Data for BaCl_2 from Bothwell and Peake

obtained for MgCl_2 and KCl and also includes the data of other investigators (1, 2, 3) for comparison. A plot of the surface tension data obtained for the KCl-MgCl_2 , $\text{BaCl}_2\text{-MgCl}_2$, and the pseudobinary systems studied as a function of MgCl_2 concentration are presented in Figure 4. The data for the binaries are also compared with those reported by other investigators (1-3). For the pseudobinaries, the surface tensions at 0% MgCl_2 were taken from the curve of Figure 3 rather than using the actual experimental data for those compositions. Figure 5 is a ternary diagram presenting the surface tension at 800°C . as a function of composition.

DISCUSSION

The surface tension data obtained for MgCl_2 and KCl (Figure 2) are 4.5 to 7% higher than those reported by other investigators. The isotherm plots for the surface tension of the KCl-MgCl_2 system exhibits the same general shape as that of Desyatnikov but is consistently higher. The major differences between the two sets of data occur in the MgCl_2 -rich mixtures. The values obtained for the $\text{BaCl}_2\text{-MgCl}_2$ binary are lower than those of Bondarenko and Strelets

from 0 to 65% MgCl_2 but higher than his from 65 to 100% MgCl_2 . The data for the KCl-BaCl_2 system are in good agreement with those of Bothwell and Peake but are slightly higher.

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