Heat Content, Specific Heat, and Heat of Melting of Magnesium Alloy AZ-80 from 280° to 1080° K.

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A KNOWLEDGE of the physical properties of metals and alloys is essential for the proper engineering of their production and fabrication facilities. Thermal properties are an important part of this information.

The heat content, $H_T - H_{298.15}$, of magnesium alloy AZ-80 has been measured in the range 280° to 1080° K. by the method of mixtures known as the drop method. From experimental data, enthalpy and specific heat equations have been derived and the heat of melting has been determined.

EXPERIMENTAL

Equipment. The copper block drop calorimeter used in this investigation is similar to the one described by Southard (*5*). A platinum–10% rhodium alloy wire (No. 20 B. and S. gage) was wound on an Alundum furnace core (1⅛-inch i.d., 20 inches long) with windings so spaced that a 2-inch isothermal zone was obtained near the center of the furnace. Furnace profile measurements at about 480°, 990°, and 1390° C. indicated this 2-inch zone to be isothermal within 0.7° C.

The temperature of the encapsulated sample is measured with a platinum *vs.* platinum–10% rhodium thermocouple which has been calibrated at the gold point (1063.0° C.). Corrections are assumed to be linear. Both the sample capsule, which is ¾-inch in o.d. and 1¼ inches long and the hot junction of the thermocouple, which nearly touches the top of the capsule, are suspended in the isothermal zone of the furnace.

The temperature of the copper calorimeter block is measured by a Maier bridge thermometer (*2*).

Material. The sample of magnesium alloy AZ-80 (Metallurgical Laboratory, The Dow Chemical Co., Midland, Mich.) had a composition of 8.0 weight % aluminum, 0.55 weight % zinc, and 0.14 weight % manganese as determined by emission spectroscopy. A 9.674-gram cylinder of the alloy was sealed in a Type 430 stainless steel capsule (5.928 grams) by arc welding under 8 cm. of mercury helium pressure.

Enthalpy. The correction for the heat content of the stainless steel capsule and heat loss during the drop was obtained from a series of empty capsule measurements. Experimental data were smoothed graphically by smoothing the first differences and the smoothed enthalpy was plotted *vs.* temperature. The "can corrections" applied to subsequent data were read directly from this graph. No attempt was made to fit the curve with an equation because of the change in curvature at the Curie point which appears around 940° K.

To check the accuracy of the apparatus, the enthalpy of α-aluminum oxide (*1*) was also determined, using the same stainless steel capsule.

RESULTS

The observed enthalpies of α-aluminum oxide (Table I) are compared with values calculated from the work of Furukawa, Douglas, McCoskey, and Ginnings (*1*).

The observed enthalpies of the alloy sample are presented in Table I. Below the solidus temperature of 781° K., the observed data were smoothed graphically by smoothing the first differences. An equation approximating observations was then derived from the smoothed data in the manner suggested by Shomate (*4*). The specific heat at 298.15° K., 0.234 cal. per gram per degree, required in the derivation was obtained from the slope of the enthalpy *vs.* temperature curve at 298.15° K.

Table I. Comparison of Observed and Calculated Enthalpy Values of $\alpha\text{-}Al_2O_3$[a] and Magnesium Alloy AZ-80

T, ° K.	$H_T - H_{298.15}$, Cal. G.$^{-1}$		Dev., Obsd. – Calcd.	% Dev. from Calcd.
	Obsd.	Calcd.		
		$\alpha\text{-}Al_2O_3$		
285.4	−2.25	−2.32	+0.07	+3.0
457.2	33.78	34.44	−0.66	−1.9
657.4	85.76	85.90	−0.14	−0.16
897.6	153.46	153.17	+0.29	+0.19
1057.7	199.58	199.81	−0.23	−0.12
	Magnesium Alloy AZ-80			
283.1	−3.39	−3.49	+0.10	+2.9
319.0	4.96	4.92	+0.04	+0.81
387.9	21.68	21.77	−0.09	−0.42
426.3	31.52	31.50	+0.02	+0.06
497.1	50.08	49.98	+0.10	+0.20
578.5	72.33	72.06	+0.27	+0.37
614.0	82.04	81.94	+0.10	+0.12
667.8	97.11	97.20	−0.09	−0.09
753.2	121.74	122.10	−0.36	−0.30
781	Solidus	130.39'		
794.2	138.03			
839.3	172.04			
881	Liquidus	232.35	...	...
901.0	239.19	239.19	0.00	0.00
923.1	246.41	246.70	−0.29	−0.12
951.7	257.62	256.46	+1.16	+0.45
1012.4	277.19	277.19	0.00	0.00
1062.5	294.19	294.25	−0.06	−0.02

[a] Calculated values from (*1*).

For the solid from 280° to 781° K.:

$$H_t - H_{298.15} = 0.21885T + 5.3321 \times 10^{-5}T^2 + 1479.4T^{-1} - 74.952$$

cal. per gram (within 0.5% of the observed values from 380° to 781° K.; 3% from 280° to 380° K.).

Differentiating,

$$c_p = 0.21885 + 10.6642 \times 10^{-5}T - 1479.4T^{-2}$$

cal. per gram per degree. Above the liquidus temperature of 881° K., the heat content was considered to be linear with temperature. For the liquid from 881° to 1080° K.:

$$H_T - H_{298.15} = 0.34112T - 68.177$$

cal. per gram (within 0.5% of the observed values) and

$$c_p = 0.341$$

cal. per gram per degree.

Percentages given in parentheses indicate the fit of the equations to observed data as given in Table I and do not necessarily indicate the accuracy of the calculated values. Graphically smoothed enthalpy and specific heat quantities at 20° K. intervals are given in Table II.

Solidus and liquidus temperatures of 781° and 881° K. were read from a phase diagram of the Al-Mg system (*3*) considering the subject alloy to be essentially binary. Consequently there is some uncertainty in the choice of these temperatures, and the present investigation is not detailed enough to give an independent check of the figures. A change in the solidus and/or liquidus temperature would affect the heat of melting, of course. Therefore, the heat of melting is here defined as the heat required to change the solid at 781° K. to the liquid at 881° K. and is 102.4 ± 0.4 cal. per gram.

Table II. Smoothed Enthalpy and Specific Heat Values of Magnesium Alloy AZ-80

T, ° K.	$H_T H_{298.15}$, Cal. G.$^{-1}$	c_p, Cal. G.$^{-1}$ Deg.$^{-1}$	T, ° K.	$H_T - H_{298.15}$, Cal. G.$^{-1}$	c_p, Cal. G.$^{-1}$ Deg.$^{-1}$
300	0.42	0.234	700	106.48	0.288
320	5.15	0.238	720	112.24	0.289
340	9.96	0.242	740	118.03	0.290
360	14.84	0.245	760	123.84	0.291
380	19.79	0.249	780	129.67	0.292
400	24.81	0.252	Solidus		
420	29.89	0.256	781	129.96	
440	35.04	0.259			
460	40.25	0.262	Liquidus		
480	45.52	0.265	881	232.35	
500	50.84	0.268	900	238.83	0.341
520	56.21	0.270	920	245.65	0.341
540	61.63	0.273	940	252.48	0.341
560	67.10	0.275	960	259.30	0.341
580	72.61	0.277	980	266.12	0.341
600	78.16	0.279	1000	272.94	0.341
620	83.75	0.281	1020	279.76	0.341
640	89.38	0.283	1040	286.59	0.341
660	95.05	0.284	1060	293.41	0.341
680	100.75	0.286	1080	300.23	0.341

LITERATURE CITED

(1) Furukawa, G.T., Douglas, T.B., McCoskey, R.E., Ginnings, D.C., *J. Research Natl. Bur. Standards* **57**, 67–82 (1956).

(2) Maier, C.G., *J. Phys. Chem.* **34**, 2860–8 (1930).

(3) Raynor, G.V., *Inst. Metals (London)*, Annotated Equil. Diagram No. 5, Second Reprint, December 1949.

(4) Shomate, C.H., *J. Phys. Chem.* **58**, 368–72 (1954).

(5) Southard, J.C., *J. Am. Chem. Soc.* **63**, 3142–6 (1941).

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Spectrophotometrically Determined Ionization Constants of Derivatives of Symmetric Triazine

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ULTRAVIOLET absorption spectra of ions as well as of neutral molecules in aqueous solution may be readily obtained. Extensive and profound changes in the spectra of ions with respect to the spectra of neutral molecules indicate similar important changes in the bonding of the conjugated or resonating system (chromophore) of the molecule. These effects have been used in studying the spectra and structures of 2,4,6-triamino-*s*-triazine (melamine) and its hydrolysis products and their acyclic analogs (*8*). Since changes were known to occur in the spectra of various *s*-triazine derivatives upon ionization, it was desired to examine these effects in detail and to determine the ionization constants which are reported here.

APPARATUS

Ultraviolet absorption spectra were obtained by use of a Cary Model 11 spectrophotometer and a Warren-Spectracord Model 3000. The Spectro-Titrimeter attachment to the Cary instrument has been described (*11*). This circulates the solution being titrated through a quartz absorption cell in the sample compartment of the spectrophotometer, permitting spectra to be obtained as a function of pH value, the latter being read from a line-operated pH meter. Absorbance (at a wave length where changes with pH are pronounced) is then plotted manually *vs.* pH values. At the point where the observed absorbance is halfway between values for the entities (neutral molecule and ion, or two ions), the pH is equal to the pK_a (or $14 - pK_b$). In cases where the spectra of one entity cannot be determined, the method of Rosenblatt (*14*) was applied to the data.

Several modifications of the original design of the Spectro-Titrimeter were made in order to incorporate a more stable line-operated pH meter (Leeds & Northrup) and to allow easier interchange of cells of various light path lengths. Further alterations were made to render the system as all-glass as possible by elimination of plastic tubing (except for very short lengths holding together the butted ends of the quartz and glass tubing). A Fisher Volustat was equipped with a 20-ml. syringe to replace the original wheel and syringe arrangement and to obtain a higher pumping rate (500 ml. per minute). Ball and socket joints permitted easy assembly and cleaning of the system. Cell lengths of 1, 10, and 50 mm. light path length were used. Solutions were dilute, generally in the range of 10^{-3} to 10^{-5} M. (The approximate concentrations used may be derived from absorptivities and cell lenghts.) Solutions of 1, 0.1, and 0.01N HCl and NaOH were generally used for the titrations, with more concentrated solutions in the extreme pH values.

A typical set of curves obtained from the Spectro-Titrimeter and the resulting plot of absorbance *vs.* pH shown in Figure 1, is reproduced from King and Hirt (*11*).

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