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

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.

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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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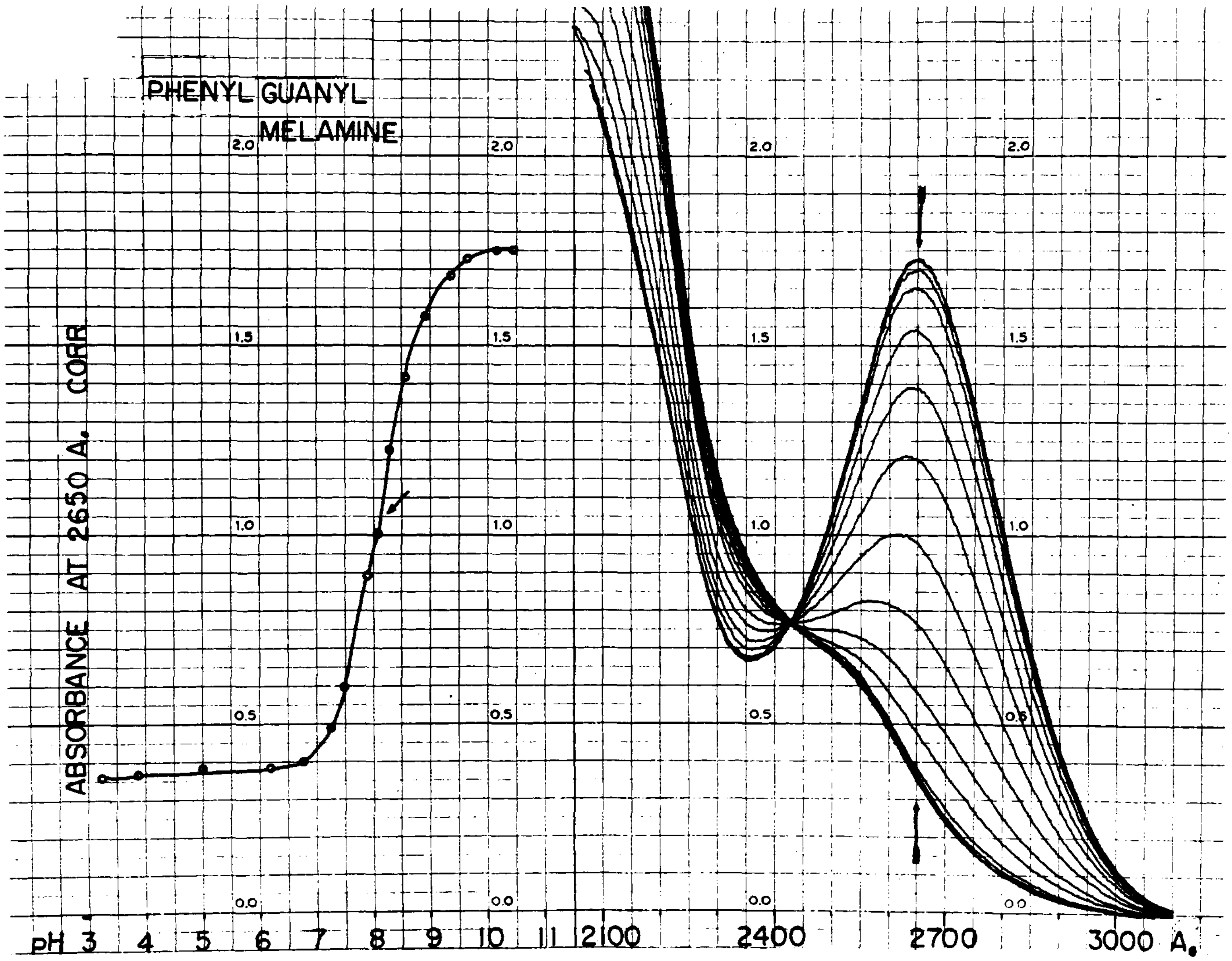

Figure 1. Cary trace of the titration of phenylguanyl melamine and plot of absorbance vs. pH

RESULTS

Data summarized in Table I include empirical formula, name, wave length in Angstroms, and absorptivity of the longest wave length absorption band (which was used for absorbance *vs.* pH plots), ionic forms involved, the pK_a or pK_b, and a reference to the literature, wherever applicable.

DISCUSSION

The structures and spectra of the melamine-to-cyanuric acid system have been discussed in detail (*8*). A comparison of these compounds with their thio analogs (Table I) shows that the thio compounds are uniformly weaker bases than their oxygen-containing analogs. In general, they are believed to have similar structures, particularly thioammeline (*17*). Some anomalies exist for thioammelide, however, which are not pertinent to this article.

All amino-substituted *s*-triazine derivatives are believed to form positive ions in the same manner as melamine (*8*), by assuming a structure with one exocyclic double bond to an $=NH_2^+$ group.

Two compounds which are not derivatives of symmetric 1,3,5-triazine, but of asymmetric 1,2,4-triazine were examined for comparison. These have different spectra, with the band arising from the nonbonding nitrogen electron transition ($n \rightarrow \pi$) well separated from the benzenoid transition (*7*). Comparison of 3-amino-*as*-triazine with 2-amino-*s*-triazine (pK_b 9.9 *vs.* 11.1) shows the asymmetric derivative to be a somewhat stronger base. The parent compound, *s*-triazine, decomposes rapidly in aqueous solution (*5*), but its pK_b is estimated to be greater than 13 from nonaqueous titrations and hydrolysis studies.

Fellig (*3*) reported "no ultraviolet spectrum" for triuret. This is correct for the neutral molecule, which likely exists in the tricarbonyl form. The negative ion, however, showed a very strong band at 2250 A., indicating a conjugated structure similar to that of biuret (*8*).

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Table I. Spectral Data and Spectrophotometrically Determined Ionization Constants of Derivatives of s-Triazine

Empirical Formula	Compound Name	Ionic Form	Wave Length, A.	Absorptivity	pK_a	pK_b	Ref.	Type of Information^{a}
$C_2H_4N_4$	Cyanoguanidine (dicyandiamide)	Neutral	2140	167	...	14.4	(*16*)	S^{b}
		Positive	...	...	...	...		
$C_3H_4N_4$	3-Amino-*as*-triazine	Neutral	3210	21	...	9.9	(*7*)	S^{c}
		Positive	3000	0.6	...	...		
$C_3H_4N_4$	2-Amino-*s*-triazine	Neutral	2610	22	...	11.1	(*6*)	S^{d}
		Positive	2500	140	...	...		
$C_3H_3N_3O_3$	Cyanuric acid	2nd negative	2200	49	~15	...	(*8*)	*S*, *C*
		1st negative	2140	79	10.6	...		
		Neutral	...	...	6.5	...		
$C_3H_3N_3S_3$	Trithiocyanuric acid	2nd negative	3070	190	...	...	(*1*)	*P*
		1st negative	3270	150	8.0	...		
		Neutral	2960	260	4.96	...		
$C_3H_4N_4O_2$	Ammelide	2nd negative	...	...	...	...	(*8*)	*S*, *C*
		1st negative	2260	76	13.5	...	(*4*)	*S*, *P*
		Neutral	2220	110	6.9	12.2		
		Positive	...	...	...	...		
$C_3H_4N_4S_2$	Dithioammelide	Negative	2680	149	...	...	(*9*)	*P*
		Neutral	2820	170	8.2	10.4		
		Positive	2700	169	...	...		
$C_2H_5N_5$	2,4-Diamino-*s*-triazine (formoguanamine)	Neutral	2580	39	...	10.1	(*2*)	C^{e}
		Positive	2350*g*	50	...	...	(*6*)	*S*
$C_3H_5N_5O$	Ammeline	Negative	2300*g*	...	...	...	(*8*)	*S*
		Neutral	2300	60	9.4	9.5	(*4*)	*S*, *P*
		1st positive	2300	148	...	~16		
		2nd positive	...	...	...	...		
$C_3H_5N_5S$	Thioammeline	Negative	2680	149	...	...	(*17*)	*P*, *C*
		Neutral	2820	170	8.2	10.4		
		Positive	2700	169	...	...		
$C_3H_6N_4O_3$	Triuret	Negative	2250	123	...	...	(*3*)	P^{b}
		Neutral	...	...	10.1	...		
$C_4H_4N_6S$	2,4-Diamino-6-thiocyanato-*s*-triazine	Negative?	2670	...	...	...	...	^{f}
		Neutral	2770	...	8.5	10.9		
		Positive	2690	...	...	...		
$C_4H_5N_7O$	4,6-Diamino-*s*-triazine-carbamonitrile (cyanomelamine)	Neutral	2460	144	...	7.3	(*10*)	*P*
		1st positive	2530	130	...	12.9		
		2nd positive	2420*g*	109	...	...		
$C_4H_6N_4O$	4-Amino-6-methyl-*s*-triazin-2-ol (acetoguanide)	Negative	2480	40	...	...	(*13*)	*P*
		Neutral	2350*g*	42	9.2	10.9		
		Positive	2450	61	...	...		
$C_4H_7N_5$	2,4-Diamino-6-methyl-*s*-triazine (acetoguanamine)	Neutral	2540	27	...	9.4	(*6*)	*S*
		Positive	2450*g*	52	...	...		
$C_4H_7N_5O$	4,6-Diamino-*s*-triazine-2-methanol	Neutral	2560	31	...	9.9	...	
		Positive	2560*g*	16	...	...		
$C_5H_7N_5O_2$	4,6-Diamino-*s*-triazine-2-acetic acid	Neutral	2620	18	...	9.6	...	
		Positive	2520*g*	18	...	...	...	
$C_4H_8N_6$	Methylmelamine	Neutral	2360*g*	...	...	8.9	(*6*)	*S*
		Positive	2360	93.5	...	...		
$C_5H_8N_4$	3-Amino-5,6-dimethyl-*as*-triazine	Neutral	3170	27	...	10.3	(*7*)	S^{c}
		Positive	2950	13	...	...		
$C_6H_9N_{11}$	2,2′-Iminobis(4,6-diamino-*s*-triazine) (melam)	Neutral	2900	29	...	12.1	...	
		Positive	2960	11	...	...	...	
$C_6N_{11}N_5O$	2,4-Diamino-6-propoxy-*s*-triazine	Neutral	2370*g*	14	...	10.3	...	
		Positive	2280*g*	51	...	...	...	
$C_9H_8N_4O$	4-Amino-6-phenyl-*s*-triazine-2-ol (benzoguanide)	Negative	2420	171	...	...	(*13*)	*P*
		Neutral	2540	170	8.1	11.0		
		Positive	2750	195	...	...		
$C_9H_9N_5$	2,4-Diamino-6-phenyl-*s*-triazine (benzoguanamine)	Neutral	2550	90	9.9	...	(*12*)	*S*
		1st positive	2480	80	12.1	...		
		2nd positive	2550	89	...	...		
$C_9H_9N_5O$	2,4-Diamino-6-phenoxy-*s*-triazine	Neutral	2390*g*	15	...	11.2	(*15*)	*P*
		Positive	2390	42	...	...		

Type of information [a] *S* = Spectral or structural data. *C* = Ionization constant data. *P* = Preparation or property description. [b] Acyclic compounds included for comparison. [c] Derivative of asymmetric or 1,2,4-triazine. [d] Decomposes in acid solutions. [e] Value (*2*) in error because of a misprint; the correct value is in agreement. [f] Solubility was too low to permit accurate measurements of absorptivity values, but ionization constants were obtained from absorbance *vs.* pH plots. *g* = "Shoulder" or partially resolved band.

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