New Thermodynamic Data for Liquid Aluminum-Magnesium Alloys from emf, Vapor Pressures, and Calorimetric Studies

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(Submitted 6 June 1997; in revised form 8 August 1997)

Experimental thermodynamic studies of liquid Al-Mg alloys have been performed by several methods resulting in: (1) Mg activities from galvanic cells with liquid electrolytes at temperatures from 910 to 1070 K, at X_{Mg} = 0.1 to 0.7 and for the dilute range when X_{Mg} = 0.0126 to 0.1430 at 927 K; (2) Mg activities from the emf method with solid CaF_2 electrolyte at temperatures 921 to 1093 K, with concentrations X_{Mg} = 0.05 to 0.9; (3) Mg activities from vapor pressure measurements (Knudsen effusion method) at temperatures ranging from 722 to 1188 K, at X_{Mg} = 0.0424 to 0.8885. Vapor pressures of pure solid Mg at temperatures 674 to 851 K. In addition, liquidus temperatures for Mg- and Al-rich alloys were obtained; and (4) Partial and integral enthalpies from reaction calorimetry at 1023 K, starting from pure Mg bath at concentrations, X_{Al} = 0.066 to 0.499, and starting from pure Al bath at X_{Mg} = 0.522 to 0.906. The mutual consistency of these four sets of data was analyzed. New results together with the selected thermodynamic information reported in literature were optimized to describe the liquid phase with the Redlich-Kister equation, as a preliminary step for phase diagram calculations of the Al-Mg system.

1. Introduction

The Al-Mg system, its thermodynamic properties, and phase equilibria are important for the production of light, multicomponent alloys. Also, the activity of Mg plays an important role in producing cast alloys from secondary materials; these usually contain an excess of Mg arising from chlorination or vacuum treatment.

Extensive thermodynamic data are available in the literature for liquid Al-Mg alloys, but results from various techniques are not in agreement. An example of Mg activities from various references is presented in Fig. 1. This is due to the fact that the thermodynamic properties of liquid Al-Mg alloys exhibit only small negative deviations from ideal behavior and are difficult to measure with high accuracy because in calorimetric studies only small heat effects are obtained and in emf methods difficulties are encountered in establishing equilibrium at constant temperature.

The main purpose of this multitechnique research was to determine consistent thermodynamic data among participating laboratories for the liquid phase and to use these results with the selected information from various references for an optimization and, ultimately, for phase diagram calculations.

The authors' previous phase diagram calculations for the Al-Mg system by means of the Lukas (BINGSS and BINFKT) programs has been presented during *Calphad XXIII* [94Mos]. These calculations were based on phase equilibria suggested by [81Sch] and are similar to [90Sau] and [93Zuo] and different from [82Mur], [86Lud], and [94Cha]. The main difference lies in the central range of Mg concentrations in the solid state. This is discussed in a subsequent paper dealing with phase diagram calculations that accept the description of the liquid phase of the present study with various experimental data.

2. Experimental

2.1 Galvanic Cells with Liquid Electrolytes

Two kinds of concentration cells with molten salt electrolytes were used to obtain Mg activities. The first cell:

$$Mg_{L\ or\ S}\ |\ MgCl_2\ \text{in}\ (KCl\text{-}LiCl)_{eut}\ |\ (Al\text{-}Mg)_L \qquad \text{(Eq 1)}$$

was used at alloy mole fractions of X_{Mg} = 0.1 to 0.7 and through the temperature range 910 to 1070 K. Experimental arrangements of cell 1 were the same as in previous studies on the Mg-Sn system [90Mos], whereas the arrangements in cell 2 were as in [90Mos] for Li alloys. Linear dependence of emf versus T(K) of cell 1 is shown in Fig. 2, and the parameters of least squares fit are presented in Table 1. They were used for calculations of partial Gibbs energy of Mg and partial enthalpy of Mg. In addition, measurements for Mg dilute solutions were repeated by means of cell 2:

$$Mg_L\ |\ MgCl_2\ \text{in}\ (LiCl\text{-}LiF)_{eut}\ |\ (Al\text{-}Mg)_1 \qquad \text{(Eq 2)}$$

In cell 2, emf measurements were made only at 927 K. The resulting data are also summarized in Table 1. In both cells 1 and 2, the alloy electrode was formed by melting components, 99.99% Al and 99.9% Mg or pure Al, directly in the cell. The concentration of Mg in the alloys was increased by coulomet-

Table 1 Experimentally Determined EMF Data Obtained in Cell 1 and 2 with Liquid Electrolytes

Linear equation of emf versus T(K) obtained in cell 1		emf values at 927 K obtained in cell 2	
X_{Mg}	$E = a + b \cdot T$, K	X_{Mg}	E_{927}, mV
0.1	$E = 41.1 + 0.0760 \cdot T$	0.0126	188.1
0.2	$E = 24.2 + 0.0563 \cdot T$	0.0204	165.1
0.3	$E = 37.9 + 0.0232 \cdot T$	0.0423	138.9
0.4	$E = 24.1 + 0.0226 \cdot T$	0.0520	130.3
0.5	$E = 25.3 + 0.0082 \cdot T$	0.0635	122.8
0.6	$E = 16.8 + 0.0098 \cdot T$	0.0782	116.5
0.7	$E = 8.1 + 0.0114 \cdot T$	0.1149	102.4
		0.1453	91.1

Table 2 Experimentally Determined EMF Data Obtained in Cell 3 with a Solid Electrolyte

	Linear equations of emf versus T (K)obtained in cell 3
X_{Mg}	$E = a + b \cdot T$, K
0.05	$E = 107.20 + 0.0376 \cdot T$
0.10	$E = 33.86 + 0.0344 \cdot T$
0.30	$E = 24.61 + 0.0374 \cdot T$
0.50	$E = 25.50 + 0.0133 \cdot T$
0.70	$E = 13.54 + 0.0099 \cdot T$
0.90	$E = 0.071 + 0.0064 \cdot T$

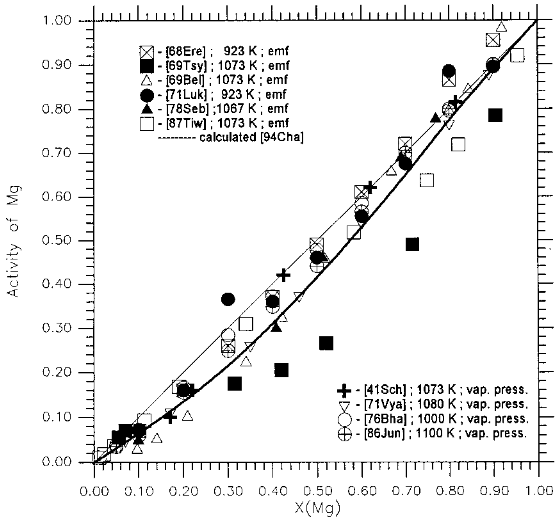

Fig. 1 Experimental data for the activity of Mg from various references. Solid line: [62Ere].

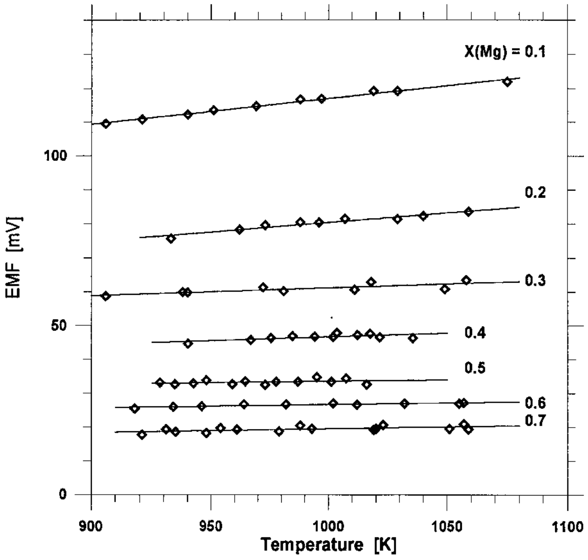

Fig. 2 Experimental emf results from cell 1.

Table 3 Experimental Data of Mg Vapor Pressure (P_{Mg}) over Liquid Al-Mg Alloys

Temperature (T), K	X_{Mg}	Vapor pressure (P_{Mg}), Pa	a_{Mg}	Temperature (T), K	X_{Mg}	Vapor pressure (P_{Mg}), Pa	a_{Mg}
Run 1				**Run 2**			
851	0.7021	48.45	0.6303	827	0.7957	35.17	0.7833
831	0.7004	30.68	0.6175	808	0.7948	21.75	0.7690
879	0.6967	92.96	0.6577	832	0.7936	40.20	0.8002
845	0.6862	41.95	0.6142	843	0.7919	51.34	0.8020
874	0.6829	82.14	0.6426	817	0.7906	28.46	0.7964
783	0.6796	9.01	0.6009	856	0.7884	70.04	0.8109
829	0.6783	28.26	0.6084	846	0.7866	55.71	0.7982
803	0.6769	14.57	0.5871	865	0.7838	86.88	0.8336
765	0.6762	5.63	0.5974	837	0.7815	44.56	0.7938
856	0.6727	51.92	0.6074	823	0.7801	31.32	0.7723
				803	0.7792	19.17	0.7847
				813	0.7782	24.89	0.7824
Run 3				**Run 4**			
870	0.8870	97.23	0.8419	722	0.6670	1.56	0.5485
881	0.8832	128.41	0.8730	767	0.6649	6.29	0.5946
891	0.8806	159.64	0.8829	737	0.6633	2.67	0.5850
874	0.8783	107.51	0.8496	778	0.6597	8.62	0.6139
879	0.8768	123.03	0.8705	733	0.6575	2.00	0.5051
885	0.8712	139.97	0.8705	752	0.6556	4.17	0.5959
865	0.8682	86.40	0.8290	794	0.6510	13.45	0.6281
Run 5				**Run 6**			
836	0.4850	23.20	0.4180	898	0.2888	44.14	0.2112
895	0.4798	86.73	0.4439	839	0.2859	11.61	0.1958
915	0.4711	129.22	0.4453	926	0.2809	76.57	0.2139
874	0.4644	53.85	0.4212	908	0.2766	51.14	0.2026
786	0.4607	5.73	0.3500	941	0.2713	100.08	0.2126
830	0.4591	17.07	0.3594	857	0.2666	16.14	0.1810
771	0.4581	3.95	0.3630	881	0.2650	28.09	0.1909
901	0.4515	83.21	0.3796	846	0.2632	12.36	0.1789
803	0.4477	8.75	0.3526	863	0.2621	18.42	0.1824
				813	0.2606	5.32	0.1673
Run 7				**Run 8**			
820	0.2515	6.96	0.1718	880	0.1673	15.34	0.1074
843	0.2468	12.30	0.1784	924	0.1631	38.07	0.1103
856	0.2410	16.31	0.1784	870	0.1598	11.64	0.0987
813	0.2332	5.54	0.1647	901	0.1558	22.72	0.1027
829	0.2273	7.95	0.1603	937	0.1511	45.13	0.1028
823	0.2240	6.75	0.1575	919	0.1476	29.95	0.0968
				929	0.1437	36.48	0.0966
				909	0.1398	23.56	0.0916
				948	0.1320	48.97	0.0922
				941	0.1258	41.40	0.0879
				927	0.1207	30.87	0.0847

(continued on next page)

ric titration as described in [90Mos]. The cells were set up in a glove box produced by M. Braun Company (Garching, Germany), with circulated Ar of high purity. Trace amounts of moisture, O and N, were continuously removed from the Ar to the level of 1 to 2 ppm by passing the gas through a molecular sieve and catalytic Cu. The circulating Ar was then directed to a separated reactor and passed over Ti sponge, kept at 850 °C to eliminate the residual N.

2.2 Galvanic Cells with Solid Electrolytes

Measurements of Mg activities of the liquid Al-Mg alloys were performed by means of the following cell:

Table 3 Experimental Data of Mg Vapor Pressure (P_{Mg}) over Liquid Al-Mg Alloys (continued)

Temperature (T), K	X_{Mg}	Vapor pressure (P_{Mg}), Pa	a_{Mg}	Temperature (T), K	X_{Mg}	Vapor pressure (P_{Mg}), Pa	a_{Mg}
Run 9				**Run 10**			
992	0.04240	31.20	0.0277	880	0.10320	9.54	0.0662
947	0.04002	13.28	0.0254	936	0.10140	28.63	0.0663
980	0.03374	19.78	0.0214	904	0.09899	14.14	0.0604
957	0.03238	12.53	0.0201	919	0.09697	18.90	0.0611
1022	0.03068	37.53	0.0206	951	0.09462	34.33	0.0614
997	0.02854	22.24	0.0183	930	0.09214	22.05	0.0574
1039	0.02554	40.75	0.0175	940	0.09012	26.98	0.0588
1016	0.02346	25.46	0.0155	969	0.08654	43.64	0.0572
984	0.02206	13.63	0.0139	948	0.08425	28.19	0.0519
1032	0.01668	22.37	0.0107	923	0.08172	16.55	0.0497
993	0.01563	11.12	0.0097	923	0.08067	16.77	0.0504
968	0.01412	6.64	0.0088	923	0.07953	16.53	0.0496
1016	0.01299	14.04	0.0086	923	0.07799	16.18	0.0486
1051	0.01166	21.66	0.0078	962	0.07463	32.13	0.0473
1110	0.00860	36.74	0.0059	934	0.07004	17.70	0.0429
1110	0.00762	32.19	0.0052	975	0.06734	36.33	0.0432
1110	0.00631	26.37	0.0042	945	0.06497	20.59	0.0408
1110	0.00522	21.78	0.0035	928	0.06241	14.18	0.0382
1110	0.00444	18.59	0.0030	993	0.05909	44.31	0.0389
1110	0.00338	14.28	0.0023	1009	0.05637	55.33	0.0376
1110	0.00262	11.08	0.0018	926	0.05266	11.39	0.0318
1110	0.00229	9.37	0.0015	952	0.04882	17.77	0.0310
1110	0.00183	7.67	0.0012	936	0.04771	12.67	0.0296
1110	0.00129	5.42	0.0009	1055	0.04125	83.29	0.0284
1188	0.00035	4.03	0.0003	1055	0.03874	78.31	0.0267
				936	0.03313	8.35	0.0195
				989	0.03117	21.45	0.0202
				1022	0.02845	34.29	0.0189

$$\mathrm{Mg,MgF_{2(L)}\ |\ CaF_2\ |\ Al\text{-}Mg,MgF_{2(L)}} \qquad \text{(Eq 3)}$$

in an experimental arrangement [95Kat] shown in Fig. 3. A single crystal rod of CaF_2 electrolyte was worked into an H-type crucible with a small hole (see Fig. 3) at the top of the wall in the lower crucible. The hole enabled the passage of Ar gas after the cell was dipped into the liquid alloy. The Ar gas was purged from the surface of the alloy through the hole to improve the contact between electrolyte and alloy electrode. This improvement was observable after the cell was immersed in the liquid alloy. The alloys were prepared by melting the desired composition of elemental metals (Mg,Al 99.98% purity) to which MgF_2 powder (99.99% purity) was added for the cell operation. Next, the cell was heated under purified Ar gas. After the alloy electrode was melted, the solid electrolyte cell was immersed into the melt and the emf measurements were performed. Both electrodes could be stirred by means of W wires. Electromotive force measurements were made through the temperature range 921 to 1093 K at Mg mole fractions ranging between 0.05 to 0.90. Experimental data for emf versus T(K) from cell 3 are shown in Fig. 4. The respective parameters of linear equations a and b are from the least squares method and are presented in Table 2.

3. Vapor Pressure Studies

Vapor pressure measurements by the Knudsen effusion method were performed on 10 starting alloy compositions for liquid Al-Mg alloys at temperatures of 722 to 1188 K at initial $X_{Mg} = 0.00035$ to 0.8870 mole fraction and for two independent measurements for pure solid Mg. The details of the experimental setup were presented by [87Bot], and they allowed preparation of the Al-Mg alloys directly in the Knudsen cell by melting components of high-purity (99.99% Al and 99.9% Mg). During vapor pressure measurements, the depletion of Mg content due to lost vapor resulted in changing composition, so both temperature and composition had to be monitored. Vapor pressure measurements under decreasing content of Mg as a function of temperature were made using a Mettler-Toledo (Greifensee, Switzerland) thermobalance that made it possible to determine the liquidus temperature for certain alloys on both the Mg-rich and Al-rich sides of the concentration range (see Table 5). Two kinds of Knudsen cells were used, both made of sintered alumina by the Frialit-Degussit Company (Mannheim, Germany). The effective area of the orifice of the coverings of Knudsen cells, equal to 0.0992 and 0.579 mm^2, were calibrated by means of Ag evaporation. During the experimental runs with the Al-Mg alloys, the assumption was

Table 4 Experimental Data of Magnesium Vapor Pressure, P^0_{Mg} over Pure Solid Mg

Temperature(T), K	Vapor pressure (P^0_{Mg}), Pa
674	0.40
697	0.89
703	1.07
708	1.32
717	1.73
724	2.24
729	2.68
732	2.69
737	3.33
746	3.94
763	7.26
769	8.61
769	8.91
784	12.60
803	20.78
803	20.93
817	30.38
827	38.80
836	48.72
851	70.32

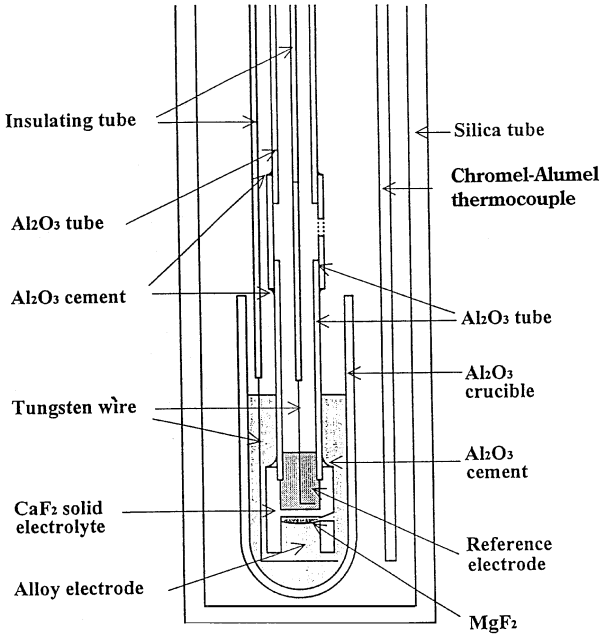

Fig. 3 Schematic diagram of cell arrangement for emf measurements in cell 3.

made that the gas phase consists solely of Mg vapor. Measured values of Mg vapor pressure, P_{Mg}, over liquid alloys are listed in Table 3 at experimental temperatures and concentrations. To calculate Mg activities from the relation:

$$a_{Mg} = \frac{P_{Mg}}{P^0_{Mg(L)}} \qquad \text{(Eq 4)}$$

one needs to know the temperature dependence of vapor pressure over pure liquid Mg, $P^0_{Mg(L)}$, which was calculated from vapor pressure measurements over solid Mg. Data for vapor pressures of pure solid Mg were measured in two independent runs and were averaged by linear equations:

$$\ln P^0_{Mg(S)} = A + B/T \qquad \text{(Eq 5)}$$

from which determination of $P^0_{Mg(L)}$ can be made:

$$-RT \ln P^0_{Mg(L)} = -RT \ln P^0_{Mg(S)} - G_{Mg(S)\rightarrow}(L)^0 \qquad \text{(Eq 6)}$$

Values of $G^0_{Mg(S)}$ were calculated assuming that $\Delta C_P = 0$, using the melting temperature and enthalpy of melting of Mg from [91Din]. Vapor pressure over the pure solid Mg are presented in Table 4. It should be added that the vapor pressure data of solid Mg of this study are about 5 to 15% lower than those in [81Glu]. However, they were used for calculations of activity of Mg in liquid Al-Mg alloys, due to the fact that vapor pressure measurements both for liquid alloys and solid Mg were performed on the same equipment, eliminating in this manner any influence of systematic errors (see Eq 4).

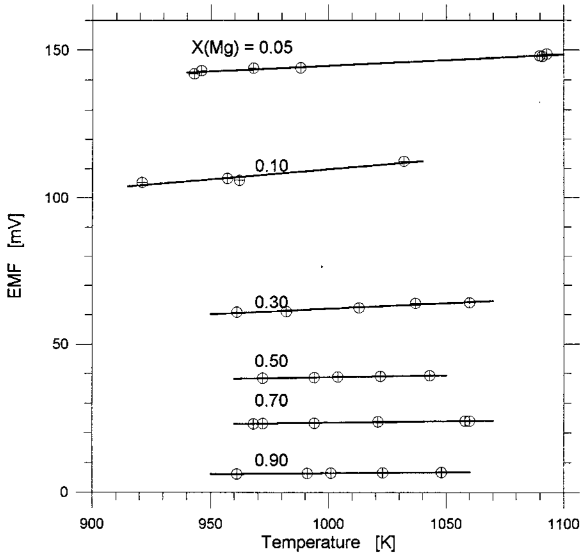

Fig. 4 Experimental emf results from cell 3.

The liquidus temperatures for Mg-rich and Al-rich parts of the Al-Mg system are presented in Table 5. They correspond moderately well with the reported phase diagram [90Sau, 93Zuo] and are used for the optimization in a subsequent paper dealing with calculations of phase equilibria.

4. Calorimetric Studies

An isothermal high-temperature mixing calorimeter, originally constructed at the Max-Planck-Institut (Stuttgart, Germany) [80Som] and copied with some modifications at the Institute of Metallurgy and Materials Science, Polish Academy of Sciences in Kraków, was used to perform three series of measurements at 1023 K. Measurements were made by dropping solid samples from ambient temperature into liquid alloys starting from pure elements. In two series, Al was dropped, and Mg was added in the third. Experiments were performed in a closed Ar atmosphere of 1 bar with continuous stirring through the various runs. Calibrations were made by adding solid samples of the bath metal before starting the measurements.

Changes in the calibration factor with the increasing amount of melt were considered in the calculations. The experimental results for liquid Al-Mg alloys are given in Table 6 together with integral and partial enthalpies calculated from the measured "heat effects." In column 5 the "heat effects" are the enthalpy differences between the sample of the concentration before and after the addition of the small amount of Al (column 4) or Mg (column 3) and include the heat cost of raising the temperature of the added component from room temperature to the bath temperature.

Partial enthalpies were calculated (column 9 and 10) by approximation dH/dn by $\Delta H/\Delta n$. For the calculations, values from column 5 were transformed to relate the partial enthalpies to the pure liquid element at 1023 K. It was made by subtracting the enthalpy difference between pure liquid Al (or Mg) at 1023 K and solid Al (or Mg) at room temperature (298.15 K). For this purpose, compiled unary data of [91Din] were used. The unknown concentration of the quotient $\Delta H/\Delta n$ was approximated as the mean of the concentration before and after the addition and is shown in column 8. The integral enthalpies of mixing (column 7) were calculated as the sum of all the transformed heat effects of the run, divided by the total amount of initial Mg (column 1) plus all added amounts of Al (column 4) (or vice versa). The integral ΔH values are shown in column 7, with corresponding Al concentrations in column 6. Partial enthalpies better illustrate the quality of a calorimetric experi-

Table 5 Experimentally Determined Liquidus Points of the Al-Mg Phase Diagram

X(Mg)	Temperature (T), K
0.8865	854
0.8851	854
0.8757	848
0.8675	843
0.2375	811
0.2231	813
0.1837	839
0.1483	859
0.0877	889

Table 6 Measured at 1023 K Heat Effects and Calculated Partial and Integral Enthalpies in Liquid Al-Mg Alloys

Measured					Calculated				
Starting amounts		Added amounts		Heat effect	Mole fraction	Integral enthalpy	Mole fraction	Partial enthalpy	
n_{Mg}, mol	n_{Al}, mol	Δn_{Mg}, mol	Δn_{Al}, mol	(Q), J	(X_{Al}), at.%	(ΔH), J/mol	(X_{Al}), at.%	H_{Al}, J/mol	H_{Mg}, J/mol
1	2	3	4	5	6	7	8	9	10
0.352829	…	…	0.026678	498	7.0	–914	3.5	–13 015	…
	…	…	0.051568	1298	18.2	–1582	12.6	–6 512	…
	…	…	0.068380	1666	29.4	–2366	23.8	–7 319	…
	…	…	0.063856	1678	37.4	–2709	33.4	–5 405	…
	…	…	0.066893	1834	44.0	–2873	40.7	–4 265	…
	…	…	0.073861	2066	49.9	–2960	47.0	–3 711	…
0.407345	…	…	0.028648	662	6.6	–563	3.3	–8 600	…
	…	…	0.055932	1296	17.2	–1466	11.9	–8 511	…
	…	…	0.073141	1872	27.9	–2063	22.6	–6 088	…
	…	…	0.071664	1876	36.0	–2451	32.0	–5 505	…
	…	…	0.072453	1876	42.6	–2790	39.3	–5 790	…
	…	…	0.066561	1827	47.5	–2913	45.1	–4 234	…
…	0.33572	0.034839	…	675	90.6	–1007	95.3	…	–10 283
	…	0.038613	…	733	82.0	–1960	86.3	…	–10 675
	…	0.030867	…	605	76.3	–2556	79.2	…	–10 058
	…	0.042848	…	1093	69.5	–2736	72.9	…	–4 149
	…	0.047690	…	1234	63.3	–2868	66.4	…	–3 783
	…	0.048992	…	1298	57.9	–2929	60.6	…	–3 164

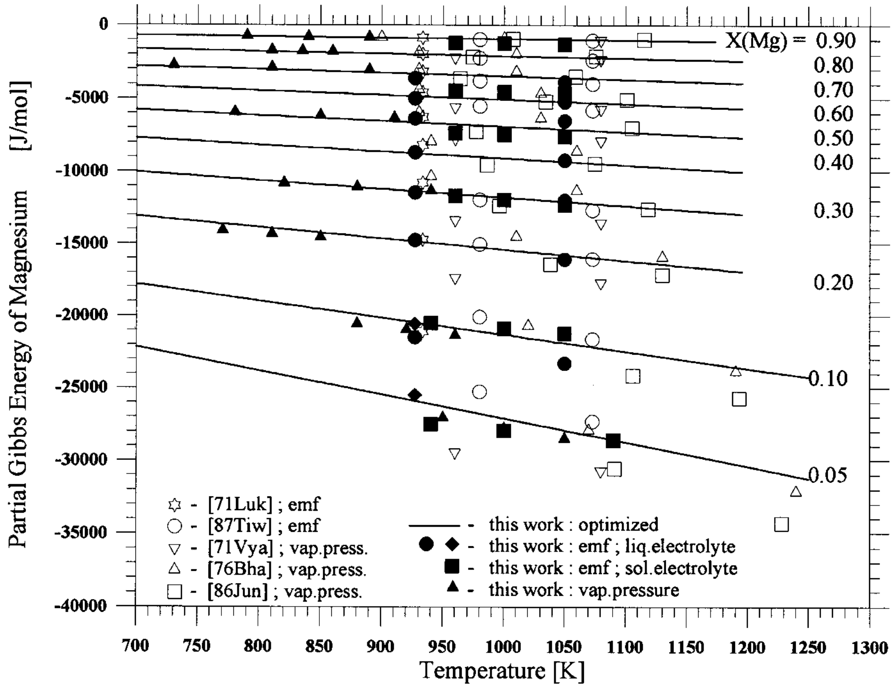

Fig. 5 Temperature dependence of partial Gibbs energies of Mg in liquid Al-Mg alloys. Solid line, calculated from coefficients presented in Table 8.

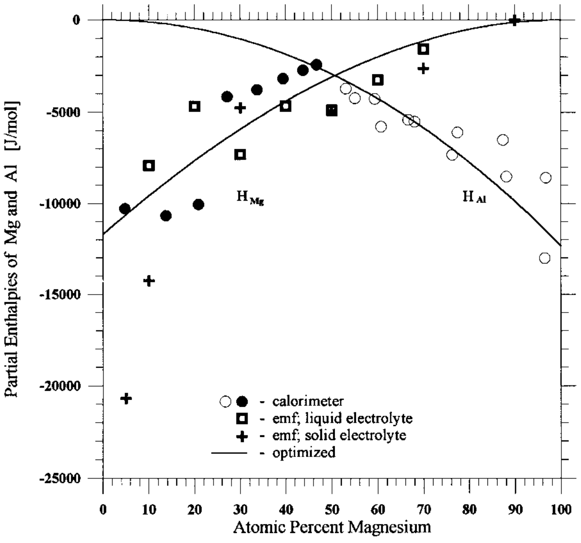

Fig. 6 Partial enthalpies of Mg in liquid Al-Mg alloys from this study. Solid line, calculated from coefficients presented in Table 8.

ment than do integral enthalpies because calculated integral enthalpies reflect not only the result of the current measurement but include accumulated scatter of all preceding measurements in the same run. Thus, the small scatter in calculated integral enthalpies may mislead the reader who wants to estimate the quality of the experiment. Even so, for purposes of comparison with literature data, the authors' integral enthalpies are presented.

For a more detailed interpretation of this type of calorimetric data, the reader is referred to a discussion by [92Luk], who has used calorimetric data in BINGSS and BINFKT programs [77Luk].

5. Discussion

Before starting with the optimization of the liquid phase, the mutual consistency of experimental data of this study should be considered. The present data are summarized in Tables 1 and 2 for the emf studies with liquid and solid electrolytes, and in Table 3 for vapor pressure measurements. Table 6 summarizes the measured "heat effects" which enable the calculations of both partial enthalpies of Mg and Al and also integral enthalpies.

The first step in comparison deals with emf and vapor pressure measurements from which partial Gibbs energies of Mg, G_{Mg}, may be calculated. Such calculation is easy from emf data, but more time consuming for vapor pressure measurements. The latter is due to the fact that the vapor pressure measurements were not performed at constant temperature or concentration, as is evident in Table 3. To calculate partial Gibbs energies of Mg at constant concentrations and to plot them with other data in Fig. 5, the vapor pressure data from

Table 7 Summary of the Experimental Data for Liquid Al-Mg Alloys

Experimental method	Value	Temperature, K	Mole fraction, % Mg	Used(a)	Reference
Calorimetry	ΔH (L)	1023	0.23 to 0.80	–	[30Kaw]
Boiling point	G_{Mg} (L)	1363 to 1566	0.20 to 0.80	–	[31Lei]
Boiling point	G_{Mg} (L)	1374 to 1427	0.65 to 0.963	–	[39Sch]
Vapor pressure transpiration	G_{Mg} (L)	917 to 1067	0.167 to 0.816	–	[41Sch]
emf	G_{Mg} (L)	723 to 913	0.10 to 0.80	–	[62Ere]
emf	G_{Mg} (L)	973 to 1103	0.003 to 0.900	–	[69Tsy]
emf	G_{Mg} (L)	993 to 1153	0.096 to 0.919	–	[69Bel]
emf	G_{Mg} (L)	933	0.10 to 0.90	+	[71Luk]
Vapor pressure	G_{Mg} (L)	1073	0.10 to 0.50	–	[71Luk]
Calorimetry	ΔH (L)	1000	0.10 to 0.80	+	[71Bat]
Vapor pressure transpiration	G_{Mg} (L)	923 to 1233	0.07 to 0.89	+	[71Vya]
Vapor pressure transpiration	G_{Mg} (L)	900 to 1245	0.05 to 0.90	+	[76Bha]
emf	G_{Mg} (L)	973 to 1173	0.10 to 0.80	–	[78Seb]
Vapor pressure boiling point	G_{Mg} (L)	960 to 1230	0.060 to 0.954	+	[86Jun]
emf	G_{Mg} (L)	973 to 1073	0.00027 to 0.955	+	[87Tiw]
Calorimetry	ΔH (L)	943 to 973	0.02 to 0.98	–	[91Aga]
emf, liquid elect.	G_{Mg} (L)	927	0.0126 to 0.145	+	This work
emf, liquid elect.	G_{Mg} (L)	910 to 1070	0.10 to 0.70	+	This work
emf, solid elect.	G_{Mg} (L)	921 to 1093	0.05 to 0.9	+	This work
Vapor pressure Knudsen	G_{Mg} (L)	722 to 1188	0.0424 to 0.8885	+	This work
Calorimetry	H_{Al} (L)	1023	0.549 to 0.965	+	This work
	H_{Mg} (L)	1023	0.047 to 0.466	+	This work

(a) Values indicated as (+) were taken to the optimization.

Table 8 Optimized Thermodynamic Parameters for Liquid Al-Mg Alloys

Redlich-Kister model

$$G^{E,\Phi} = X_{Al} \cdot X_{Mg} \cdot \sum_{i=0}^{n} (a_i + b_i \cdot T) \cdot (X_{Al} - X_{Mg})^i$$

Phase	i	a_i, J/mol	b_i, J/mol
Liquid	0	–12 002.58	8.60253
	1	319.66	0.87286
	2	0.05	…

all runs of the experiments were preliminarily described by Redlich-Kister [48Red] equations with the aid of the BINGSS program. Fitted coefficients were not used for other purposes. The mutual consistency of results of this study was confirmed in Fig. 5, in which solid lines indicate optimization including chosen data from literature. Optimization is discussed in the next paragraph.

Electromotive force methods provide direct measures of activities, and partial enthalpies of Mg can be calculated from the slopes of emf versus T(K) according to the following equations:

$$-nEF = RT \ln a_{Mg} = G_{Mg} \qquad \text{(Eq 7)}$$

$$H_{Mg} = nF\left(T\frac{dE}{dT} - E\right) \qquad \text{(Eq 8)}$$

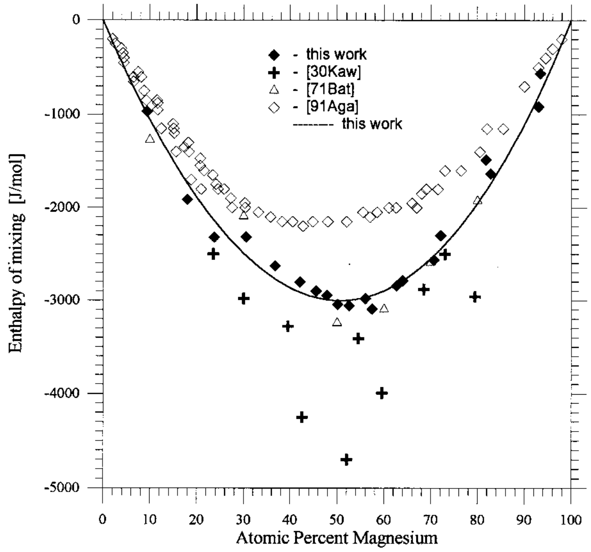

Fig. 7 Integral enthalpies in liquid Al-Mg alloys of this study compared with data from various references. Solid line, calculated from coefficients presented in Table 8.

where n is valence, F is Faraday's constant, E is emf in volts, a_{Mg}, G_{Mg}, and H_{Mg} are activity, partial Gibbs energy, and partial enthalpy of Mg, respectively, and T is temperature in Kelvin.

Partial enthalpies of both Mg and Al are also available from calorimetric studies as shown in Table 6. Figure 6 presents data for experimental partial enthalpies (points) compared with optimized solid lines. Higher deviations are observed for partial enthalpies of Mg from emf results especially in dilute Mg solutions. Partial enthalpies and entropies calculated from slopes inherently have higher uncertainties than activities or G_{Mg}, and this strongly depends on the investigated system. This comparison clearly indicates the mutual agreement of partial data of this study from various experimental techniques, which provides a starting point for comparison with data from the literature to choose the most representative set of results for optimization of the liquid phase.

6. Comparison with Other Data from Literature—Optimization of the Liquid Phase

Previously, the liquid phase of the Al-Mg system was investigated calorimetrically by [30Kaw], [71Bat], and [91Aga]. Activities of Mg in liquid alloys were determined from emf measurements of [62Ere], [69Bel], [69Tsy], and [87Tiw]. [41Sch], [71Vya], [76Bha], and [86Jun] measured the partial pressure of Mg over liquid alloys.

Presentation of Mg activities in Fig. 1 and the results of this study clearly indicate that the liquid phase of Al-Mg system exhibits slight negative deviation from ideal behavior. All the available thermodynamic data for the liquid phase of Al-Mg system are listed in Table 7. After careful analysis of all these studies, in addition to the results of the present study, data of [71Bat], [76Bha], [86Jun], [87Tiw], [71Vya], and [71Luk] were selected for an optimized thermodynamic description of the liquid phase; this is indicated by a "+" sign in Table 7. Integral enthalpies from Table 6 are plotted in Fig. 7 and compared with data of [30Kaw], [71Bat], [91Aga] and with a curve calculated from the optimized set of coefficients. The authors' experimental results are close to those of [71Bat], but in the central range of Mg concentration differ from the data of [91Aga] by about 1 kJ/mol. It is difficult to explain the difference with [91Aga] because nearly the same calorimeters were used at Stuttgart and at Krakow, and the same experimental details were kept. For the optimization the authors have chosen their data, as it was more consistent with H_{Mg} calculated from emf slopes, as well from slopes of G_{Mg} of selected literature data (Fig. 5). Chosen results were optimized by means of Lukas' BINGSS program with a Redlich-Kister formalism to describe the liquid phase. For this optimization, the authors' vapor pressure data (Table 3) together with other results from their studies as well as from the literature were considered. Because experimental data for enthalpies as well as for partial Gibbs energies are available, it was possible to independently adjust the coefficients a_i and b_i in the Redlich-Kister equations. After the trial, it was decided that three coefficients (a_0, a_1, a_2) are required to describe partial enthalpies. As for the entropy term, it was indicated that only two coefficients (b_0, b_1) are necessary and sufficient for the description of the experimental partial Gibbs energies in the Al-Mg liquid phase. The resulting binary coefficients are given in Table 8 and will be used for the calculation of the Al-Mg system in a forthcoming separate paper.

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