D_1, D_2 = coefficients of temperature change of $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$, cal/mol K
D_3 = coefficient of temperature change of α_{12}, K^{-1}
E_1, E_2 = coefficients of temperature change of $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$, cal/mol $(K)^2$
g^E = excess Gibbs free energy, cal/mol
g_{ij} = energies of interaction between an *i-j* pair of molecules, cal/mol
G_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij} \cdot \tau_{ij})$
h^E = excess enthalpy of mixing, cal/mol
p = coefficient (0 or 1) of Equations 2 and 3
q = coefficient (0 or 1) or Equations 2 and 3
Q = objective function as defined by Equation 7, cal/mol
R = gas constant, 1.98726 cal/mol K
T = absolute temperature, K
x_i = liquid-phase mole fraction of component *i*

Greek Letters

α_{ij} = nonrandomness constant for binary *i-j* interaction
ρ_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij}\tau_{ij})$
τ_{ij} = coefficient as defined by $\tau_{ij} = (g_{ij} - g_{jj})/RT$

Subscript

i = component

Superscript

E = excess

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Thermodynamic Properties of Liquid Gallium Alloys. I. Gallium-Lead

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Vapor pressure measurements have been made on liquid lead and gallium-lead alloys by use of the torsion effusion technique. From the resulting lead activities, the values for the gallium component have been calculated by the Gibbs-Duhem integration at 1143K. Wide deviations from ideal behavior have been observed. By use of previous calorimetric enthalpies, entropy values for the alloys and for their components have been derived.

Activities of the elements of Ga-Pb alloys are not well known. These parameters can be calculated using the partial free energies of formation obtained by Predel and Stein *(10)* at 923K on the basis of solubility equilibria and using calorimetric mixing enthalpies measurements. When this procedure is followed, the resulting activity values could be affected by considerable uncertainties. Therefore it has been deemed useful to determine them directly with vapor pressure measurements.

The torsion effusion method is particularly suitable for this study for the most rapid, precise reading of experimental data.

Torsion effusion measurements of lead vapor pressure, reported here, were made as an essential preliminary to the alloy studies.

Experimental

The principle of the torsion effusion technique and the apparatus details have been described elsewhere *(2, 8)*.

The relationship between the cell deflection, α, and the pressure, P, is given by:

$$P = 2K\alpha/(a_1 d_1 f_1 + a_2 d_2 f_2) \tag{1}$$

where K is the torsion constant of the suspension; a_1, a_2, d_1, and d_2 the orifice areas and distances from the axis of rotation; and f_1 and f_2 the Freeman and Searcy *(3)* correction factors for orifice geometry. Vapor pressure

Table I. Constants of Orifice Cells

	Cell 1	Cell 2
Orifice area		
a_1, 10^{-3} cm^2	9.71 ± 0.05	10.70 ± 0.05
a_2, 10^{-3} cm^2	10.25 ± 0.05	11.45 ± 0.05
Moment arm		
d_1, cm	0.648 ± 0.005	0.653 ± 0.005
d_2, cm	0.574 ± 0.005	0.641 ± 0.005
Force correction factor *(3)*		
f_1	0.570	0.601
f_2	0.578	0.621

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measurements of lead were carried out with two effusion cells made from high-purity nonporous graphite, and their constants are given in Table I.

The cell was suspended on a 30-μ-diam tungsten wire, 33.0 cm long, with a torsion constant of 0.351 ± 0.004 dyn cm rad^{-1}. The cell was heated by radiation of a tungsten wire, and its temperature was measured with a Fe-Constantan thermocouple inserted in a second cell similar to the one already mentioned and placed beneath it. To test this procedure, a preliminary experiment was carried out putting a second Fe-Constantan thermocouple in the torsion effusion cell and measuring the differences in emf values. A satisfactory agreement has been found, the error results to be ±3°C at about 1100K.

If the same effusion cell is employed in vapor pressure measurements for pure lead and for alloys and because the vapor pressure of gallium is negligibly small over the experimental temperature range *(5)*, activity values are obtained by the relation:

$$a_{\mathrm{Pb}} = \frac{P_{\mathrm{Pb}}\,(\text{alloy})}{P_{\mathrm{Pb}}\,(\text{pure})} = \frac{\alpha_{\mathrm{Pb}}(\text{alloy})}{\alpha_{\mathrm{Pb}}\,(\text{pure})}$$

so that most systematic errors in the pressure measurements are eliminated.

The Ga-Pb alloys were prepared in loco adding weighted amounts of the two components (gallium, 99.999%, Kock-Light; lead, 99.94%, Merck). At the beginning of each run, the cell was held at about 700K for many hours to degas it and to ensure a homogeneous alloy. Torsion effusion measurements of lead vapor pressure were made from 1020–1200K, and the values are plotted in Figure 1. A second-law treatment of the vapor pressure data gives the standard heat of evaporation of lead, ΔH°_{298} = 47.4 ± 0.5 kcal mol^{-1}, which is in good agreement with the third-law value, ΔH°_{298} = 46.50 ± 0.10 kcal mol^{-1}. This fact can be considered a proof of the internal consistency of the data. Both the associated errors are standard deviations. The free energy function, $-(G^\circ_T - H^\circ_{298})/T$, used for these calculations were taken from Hultgren *(5)*. The estimated average value ΔH°_{298} = 46.8 ± 0.5 kcal mol^{-1}, considering more reliable the third-law value, is in good agreement with that selected by Hultgren *(5)*, ΔH°_{298} = 46.620 ± 0.300 kcal mol^{-1}.

By use of cell 1, Ga-Pb alloys have been studied with different techniques according to their compositions. For lead-rich alloys, the deflection angle has been measured over a small temperature range, 1130–1160K. At the end of each experiment, it was possible to measure the composition variation of the sample by its weight loss which never exceeded 1 at. % lead. This procedure has been employed to study liquid alloys at 91, 88, 68, 49, and 35 at. % lead, and their respective deflections are plotted in Figure 2. Since this procedure led to a substantial composition variation for alloys with lead composition less than 20 at. %, five runs have been carried out at prefixed temperatures within the above-mentioned range, measuring the deflection angles with time, while the lead percent in the alloy is decreasing. Therefore the area of the α vs. time plot is proportional to the weight loss of the sample according to the Knudsen equation *(6, 7)*. The deflection angles corresponding to prefixed compositions have been determined on the plot mentioned above, with the initial composition of the sample known. A typical plot is shown in Figure 3. Five composition values—i.e., 18, 15, 12, 9, and 6 at. % lead—have been considered and the corresponding data are plotted in Figure 4. The error associated with composition has been estimated to be very small (<0.1%), while the one associated with the torsion angle is greater (but not superior to 4%). The activities of lead at 1143K obtained from the values plotted in Figures 2–4 are reported in Figure 5, and the gallium activities, calculated by Gibbs-Duhem integration *(12)*, are reported too. Integral entropy values have been calculated by the Gibbs-Helmholtz equation by use of the enthalpy values given by Predel and Stein *(10)* and by assumption of the

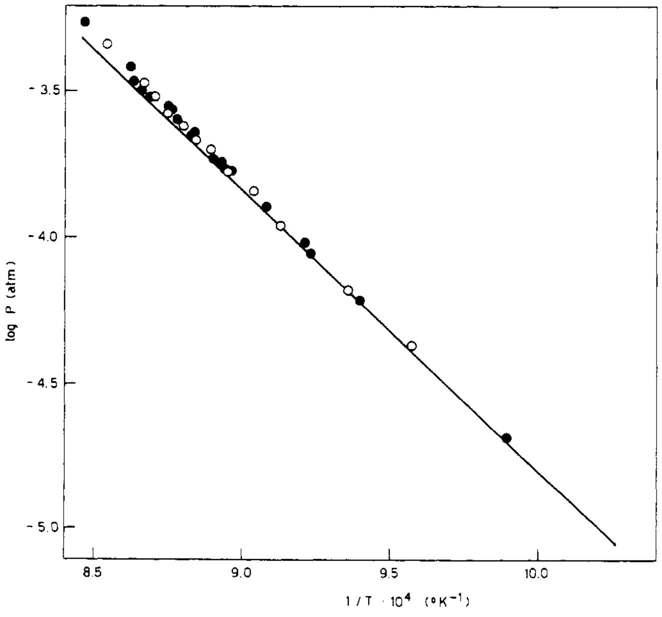

Figure 1. Vapor pressure of liquid lead
Present work: ● cell 1, ○ cell 2; Hultgren selected values (——)

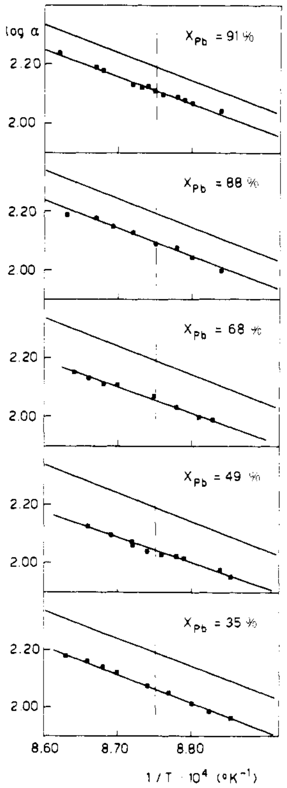

Figure 2. Plots of log α vs. $1/T$ for alloys at fixed composition (—■—) and for pure lead (——)

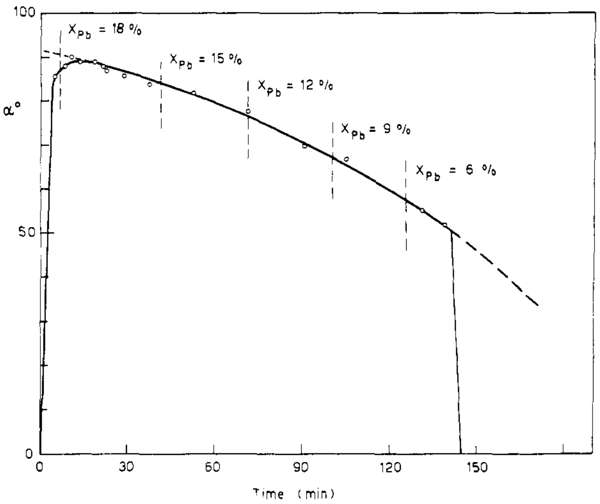

Figure 3. Typical plot of torsional angles vs. time of a low lead alloy at constant temperature (1135K)

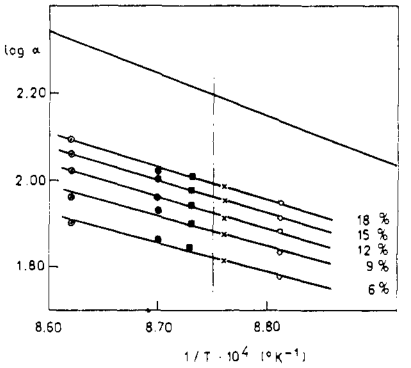

Figure 4. Plots of log α vs. $1/T$ for five alloys at constant temperatures

Table II. Thermodynamic Properties at 1143K

$X\text{Pb(l)} + (1 - X)\text{Ga(l)} = \text{Pb}_{(X)}\text{Ga}_{(1-X)}\text{(l)}$

X_{Pb}	a_{Pb}	a_{Ga}	ΔG, cal/ g-atom	ΔH, cal/ g-atom	ΔS, e.u.
0.1	0.51	0.93	−301	470	0.674
0.2	0.64	0.90	−394	730	0.983
0.3	0.70	0.87	−459	850	1.145
0.4	0.72	0.86	−500	900	1.225
0.5	0.73	0.85	−540	920	1.277
	(±0.02)	(±0.02)	(±60)	(−)	(±0.052)[a]
0.6	0.74	0.84	−568	891	1.276
0.7	0.75	0.82	−590	785	1.203
0.8	0.77	0.74	−611	645	1.099
0.9	0.86	0.37	−536	385	0.806

[a] Error calculated taking into account the uncertainties on ΔG only.

Table III. Characteristics of Metals

	Ga	Pb	Bi	Ref.
Electronegativity, eV	1.5	1.6 (II)	1.8	*4*
		1.8 (IV)		*4*
	1.6	1.8	1.9	*11*
Atomic radius, Å	1.39	1.75	1.82	*11*

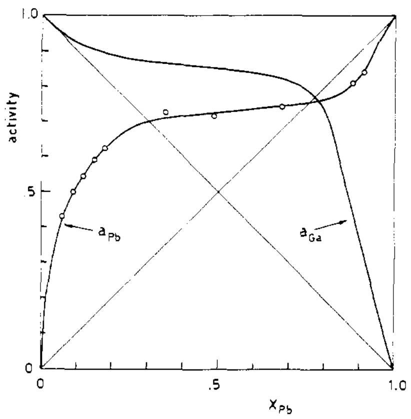

Figure 5. Activity of lead and gallium in liquid alloys vs. lead atomic fraction at 1143K

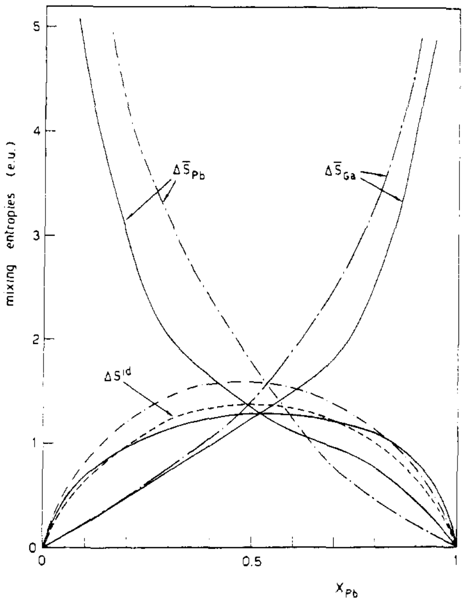

Figure 6. Integral and partial mixing entropies of liquid Ga-Pb alloys vs. lead atomic fraction at 1143K

Present work (——); Predel and Stein (—·—)

validity of the Newmann-Kopp law over the temperature range 923–1143K. Smoothed activity values and the calculated thermodynamic functions are summarized in Table II. Integral and partial molar entropies of lead and gallium are reported in Figure 6 with those of Predel and Stein *(10)* for comparison.

Discussion

The wide deviations from ideal behavior for the components of liquid Ga-Pb alloys show that a strong tendency to decompose is prevalent at 1143K. Such a tendency is due to interactions which are evident in the large miscibility gap *(1)* shown at lower temperatures.

The positive enthalpies of mixing are due, as pointed out by Predel and Stein *(10)*, to differences in the atomic radii of gallium and lead. This would in turn be responsible for positive excess entropies. But our values, reported in Figure 6, are positive only in lead-rich alloys (ΔS^{xs} = 0.159 e.u. at 90 at. % lead), and in intermediate compositions we obtain negative values even if small in magnitude (ΔS^{xs} = −0.111 e.u. at 40 at. % lead). Of course our assumption on the validity of Newmann-Kopp law over the temperature range 923–1143K could be incorrect, but heat capacities are not available in the literature. However, we think that such a correction would not substantially modify our values of excess entropy. This view is supported by comparison with the Ga-Bi system *(9)* which is analogous to the Ga-Pb system in many aspects. In fact, excess entropies are positive in bismuth-rich alloys ($\sim$0.07 e.u. at 90 at. % Bi) and negative at intermediate compositions ($-$0.2 e.u. at 30 at. % Bi). This is not surprising, because lead and bismuth are neighbors in the sixth period of the Periodic Table and have similar properties as shown in Table III. As one can see, the difference in electronegativity for Ga-Bi alloys is greater than or at least equal to that for Ga-Pb alloys. Taking into account the errors which affect the electronegativity values, one could attribute the differences of excess entropies between Ga-Bi and Ga-Pb alloys to electronic peculiarities. This seems supported by the maximum mixing enthalpy of Ga-Pb alloys which is larger than that of Ga-Bi alloys (920 and 504 cal/g-atom, respectively).

At present, we cannot regard the excess entropies of Ga-Pb alloys as more reliable than those of Predel and Stein for our assumption on Newman-Kopp law validity. Further calorimetric measurements of mixing enthalpies at 1143K should be carried out to get entropy values from direct experimental data.

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ORGANIC SECTION

Survey of Alkanone Reactivity Based on Time Required for 50% Oximation

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The 50% oximation times for 238 alkanones have been determined. Several empirical rules have been derived for estimating the 50% oximation times of many other alkanones.

The oximation studies previously reported (5) have been extended to alkanones of other structural types. For the purpose of this investigation the alkanones were divided into 25 classes (A_1–A_{12}, B_1–B_5, C_1–C_5, D, E, and F) as shown in Table I.

Results and Discussion

The 50% oximation times for 238 alkanones are listed in Table I. At least one member of each class was prepared and tested. The following empirical rules were derived from the results.

The first rule is based on the following considerations: All of the alkanones may be formally derived from 2-propanone by the successive introduction of methyl groups as illustrated in Figure 1. Although there is a well-defined exception (see Rule I), the oximation rates decrease with increasing carbon content as the arrows are followed from left to right. Conversely, the rates increase with decreasing carbon content as the arrows are followed from right to left. It must be emphasized that any number of similar diagrams may be made starting with any alkanone, thus deriving sequences with increasing or decreasing carbon content having correspondingly lower or higher oximation rates. The first rule was therefore formulated as follows:

Rule I. The successive introduction of methyl groups into an alkanone always decreases the oximation rate while the successive removal of methyl groups always increases the oximation rate. However, the successive introduction or removal of methyl groups in the R of $\mathrm{RCH_2CH_2COR}_{prim,\ sec,\ tert}$ or $\mathrm{(RCH_2CH_2)_2CO}$ has little or no effect on the oximation rate.

Several exceptions were found to the above rule. For example, ketone numbers $C_{3\text{-}4}$ and $C_{3\text{-}5}$ were markedly more reactive than the corresponding straight chain compounds, while an impure sample of the highly branched ketone $C_{3\text{-}6}$ was less reactive. Further work is required to determine the extent of these exceptions.

Rule II. Alkanones of the type RR′CHCOR″ have a lower oximation rate than the corresponding alkanone RR′CO, when R″ is any alkyl group except methyl.

The following ratios are constant enough to have predictive value, particularly ratios A and B:

Rule III.

A. $t_{50\%}\ \mathrm{R}_{prim,\ sec,\ tert}\mathrm{COC_3}/t_{50\%}\ \mathrm{R}_{prim,\ sec,\ tert}\mathrm{COC_2} = 1.35\text{–}1.62$ (1.54 av)

B. $t_{50\%}\ \mathrm{R}_{prim,\ sec,\ tert}\mathrm{CH_2CH_2COC_2}/t_{50\%},\ \mathrm{R}_{prim,\ sec,\ tert}\mathrm{CH_2CH_2COC} = 3.8$

C. $t_{50\%}\ \mathrm{R}_{sec}\mathrm{CH_2COC_2}/t_{50\%}\ \mathrm{R}_{sec}\mathrm{CH_2COC} = 6.69\text{–}8.15$ (7.6 av)

D. $t_{50\%}\ \mathrm{R}_{sec}\mathrm{COC_2}/t_{50\%}\ \mathrm{R}_{sec}\mathrm{COC} = 15.0\text{–}27.8$