The results are shown in Table XI and plotted in Figure 8. The maximum possible error in the values obtained from Equation 8 or 9 is believed less than 0.5%.

The heats of vaporization so evaluated were correlated by the least squares methods to the equation

$$\Delta H_v = -5.23241 \times 10^{-2}(t_c - t) + 1.30462 \times 10^{-4}(t_c - t)^2 + 16.2013(t_c - t)^{0.386} \quad (10)$$

Deviations between experimental values and those calculated from Equation 10 are shown in Table XI. The average absolute deviation is 0.71%, while the standard error of the regressions was found to be 0.90 cal per gram.

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NOMENCLATURE

d = molal density, g.-mole/liter
f = fugacity, atm.
ΔH_v = heat of vaporization, cal./g.
J = dimensional constant, 0.0242179 cal./ml. atm.
R = gas constant of cyclopropane, 1.9498804 atm. ml./° K.-g.
P = pressure, atm.
ΔS_v = entropy of vaporization, cal./g.° C.
T = absolute temperature, ° K.
t = temperature, ° C.
V = specific volume, ml./g.
Z = compressibility factor, PV/RT
γ = volume residual, ml./g.
ν = fugacity coefficient, f/P

Subscripts

c = critical state
g = saturated vapor state
l = saturated liquid state

LITERATURE CITED

(1) Beattie, J.A., *Proc. Amer. Acad. Arts Sci.* **69**, 389 (1934).
(2) Booth, H.S., Morris, W.C., *J. Phys. Chem.* **62**, 875 (1958).
(3) Cameron, A.E., Wichers, E., *J. Amer. Chem. Soc.* **84**, 4175 (1962).
(4) Couch, E.K., "Thermodynamic Properties of Nitrous Oxide," Ph.D. dissertation in chemical engineering, University of Texas, Austin, Tex., 1956.
(5) Hamming, R.W., "Numerical Methods for Scientists and Engineers," p. 156, McGraw-Hill, New York, 1962.
(6) "Handbook of Chemistry and Physics," 48th ed., p. F-201, Chemical Rubber Co., Cleveland, Ohio, 1968.
(7) "Handbook of Mathematical Functions," U. S. Dept. of Commerce, National Bureau of Standards, Washington, D. C., **AMS55**, 7 (1964).
(8) Hellwig, L.R., "Pressure-Volume-Temperature Properties of Sulfur Dioxide," Ph.D. dissertation in chemical engineering, University of Texas, Austin, Tex., 1955.
(9) Hsu, C.C., "Pressure-Volume-Termperature Measurements of Methyl Chloride and its Thermodynamic Properties," Ph.D. dissertation in chemical engineering, University of Texas, Austin, Tex., 1963.
(10) Keyes, F.G., *Proc. Amer. Acad. Arts Sci.* **68**, 505 (1933).
(11) Lin, D.C.-K., "Volumetric and Phase Behavior of Cyclopropane and Its Thermodynamic Properties," Ph.D. dissertation in chemical engineering, University of Texas, Austin, Tex., 1969.
(12) Matheson Co., Inc., East Rutherford, N. J., "Matheson Gas Data Book," p. 129, 1961.

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Liquid-Vapor Equilibria in the Sodium-Lead System

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Total vapor pressure measurements were made on liquid Na-Pb alloys of compositions from 0.15 to 0.90 atom fraction sodium, and at temperatures from 480 to 998° C. Transpiration experiments were done at 853° C on liquids containing 0.1, 0.2, and 0.3 atom fraction sodium. Activities for sodium were calculated directly from the data, and activity coefficients for lead were obtained by a graphical Gibbs-Duhem integration.

Thermodynamic information for the sodium-lead system as determined from measurements on liquid-vapor equilibria is reported in a sequel to our earlier study of the sodium-bismuth system (*4*). An "interpretation" of the data in terms of a quasi-ideal solution model is possible, and has been applied successfully. However, the unsupported assumption of the treatment, that of a pseudo-compound in a liquid metal, becomes very tenuous in the case of the sodium-lead system, and the treatment is omitted here, in order not to lend apparent credence to the assumption. Our position is one of suspended judgment; if and when independent measurements confirm the existence and nature of the particular intermetallic species involved in a system, a meaningful quasi-ideal solution treatment may be possible.

EXPERIMENTAL

Vapor-liquid equilibrium data were obtained from total vapor pressure measurements made by the quasi-static method (*3*) and from transpiration experiments performed in equipment described earlier (*4*). The total pressure measurements provided vapor pressures as a function of

Table I. Total Vapor Pressure Data for Na-Pb System[a]

Liquid Composition, Atom Fraction Sodium	A	B	Root-Mean-Square Error in Log P	P(1126° K), Torr	No. of Data Points	Temp. Range, ° K
0.152	6541.24 ± 190.44	6.3844 ± 0.1549	0.0113	3.76 ± 0.09	14	1181-1260
0.301	6621.37 ± 72.43	7.1010 ± 0.0637	0.0087	16.6 ± 0.3	11	1067-1224
0.399	6656.69 ± 43.37	7.4619 ± 0.0421	0.0108	35.5 ± 0.9	23	948-1172
0.499	6348.62 ± 15.43	7.6032 ± 0.0146	0.0038	92.3 ± 0.8	24	958-1140
0.603	5981.29 ± 32.51	7.5021 ± 0.0302	0.0042	155 ± 1	14	1015-1146
0.700	5744.27 ± 18.26	7.5070 ± 0.0186	0.0058	254 ± 3	10	837-1147
0.800	5423.23 ± 25.31	7.3865 ± 0.0230	0.0017	372 ± 1	10	1063-1144
0.900	5310.81 ± 10.58	7.4257 ± 0.0111	0.0069	512 ± 8	30	754-1103

[a] Vapor pressures expressed as $\log P(\text{torr}) = -A/T + B$.

Table II. Transpiration Method Measurements on Na-Pb System at 1126° K

Liquid Composition, Atom Fraction Sodium	Partial Pressures, Torr			Total Pressure, Torr	Vapor Composition, Atom Fraction Sodium	No. of Data Points
	p_{Na}	p_{Na_2}	p_{Pb}			
0.300	16.4	0.11	0.079	16.6 ± 0.6[a]	0.996	5
0.200	6.76	0.018	0.104	6.88 ± 0.21	0.985	5
0.100	2.24	0.002	0.119	2.36 ± 0.15	0.950	4

[a] Standard deviations.

temperature (480° to 998° C) and composition (0.15 to 0.90 atom fraction sodium). The transpiration experiments, performed at 853° C only, provided vapor density data for the liquid compositions 0.10, 0.20, and 0.30 atom fraction sodium; from these data it was evident that for liquids containing more than 0.30 atom fraction sodium, the vapor would contain less than 0.004 atom fraction lead. Therefore, in total vapor pressure measurements on liquids containing more than 0.30 atom fraction sodium, the amount of lead in the vapor was regarded as negligible, so that the measured pressure could be taken as sodium vapor pressure.

The transpiration equipment was constructed of Type 316 stainless steel, except for the tantalum collector tubes. The liquid sample was at the bottom of a 5-cm-diameter well, sealed at the top with a cover plate. By means of O-ring sealed fittings, a gas-tight passage was provided through the cover plate for a thermowell-stirrer, a carrier gas inlet tube, and a vapor sample collection tube. The volume of vapor space that had to be saturated was restricted with a canister. Carrier gas flowed through the apparatus during the heatup period in such a way that spurious collection of sample was avoided.

The transported sample (composed of sodium and lead) in the transpiration experiments was removed for quantitative determination. Repeated flushing with water dissolved and leached the sodium and part of the lead, giving a solution that was then acidified with standard acid and back-titrated. A precipitate of tantalic acid (from the tantalum collection tubes) formed when the acid was added. Lead occluded in this precipitate was determined by polarographic analysis. The main portion of lead was removed from the tantalum tube by washing with 3*N* nitric acid. Aliquots of this solution were analyzed flame photometrically to determine sodium that escaped the initial water washing because of occlusion in lead. Other aliquots were analyzed for lead using an EDTA titration method (*10*); excess standard $MgCl_2$ solution was added and the titration was performed in the presence of tartrate and cyanide at pH 10, using Eriochrome Blue Black B indicator.

The Chromel-Alumel thermocouples used in the experiments were checked for accuracy by comparison with standardized Pt-Pt:10% Rh thermocouples in a thermal analysis apparatus. Further details of apparatus and technique are described (*4*).

RESULTS

The data from the quasi-static measurements of total vapor pressure are presented in Table I in the form of constants (obtained from a computer-fitted least-squares treatment) in the equation $\log P\ (\text{torr}) = -A/T + B$. The standard deviations for *A* and *B* are given, as well as the root mean square error in log *P*. Also listed is the pressure at 1126° K, calculated from each equation. The results from the transpiration experiments at 1126° K are listed in Table II. The lead vapor was treated as monatomic, but the sodium vapor was treated as a mixture of monatomic and diatomic species. Values for the partial pressure of monatomic sodium, p_{Na}, were necessary for calculation of the activity of sodium in the various melts. The procedure for calculating these values was outlined previously (*4*); for the gas phase equilibrium, $Na_2 \rightleftharpoons 2Na$, at 1126° K, the equilibrium constant was taken to be 3.26 on the basis of data for pure sodium found in Sittig's compilation (*9*). From the Sittig compilation, too, the value of 481.4 torr was taken for the partial pressure of monatomic sodium over pure liquid sodium p°_{Na}, at 1126° K. The resulting values for p_{Na}, activity, and activity coefficients for sodium are given in Table III, together with the activity coefficients and activities for lead in the liquid phase that were obtained from a graphical Gibbs-Duhem integration. A pressure-composition phase diagram for the system at 1126° K is shown in Figure 1.

The temperature range of total vapor pressure measurements extends to a low enough temperature in the case of $x_{Na} = 0.900$ so that a short extrapolation (56°) to the temperature 698° K was possible in order to compare our results with the values compiled by Hultgren *et al.* (*6*). Our vapor pressure equation from Table I gave a total vapor pressure of 0.656 torr at 698° K. Using Sittig's (*9*) data to evaluate the sodium monomer-dimer equilibrium constant at this temperature, we calculated, finally, an activity for sodium of 0.926. Hultgren *et al.*'s value is 0.867. The agreement is satisfactory.

Where comparison is possible, the agreement between our transpiration and total pressure data is good. A direct comparison between experimental data for the sodium component is possible only for the composition of 0.300 atom fraction sodium. Here, the total vapor pressure obtained

Table III. Activities and Activity Coefficients for Sodium-Lead System at 1126° K

Atom Fraction Sodium, x_{Na}	Sodium Activity, a_{Na}	Sodium Activity Coefficient, γ_{Na}	Lead Activity, a_{Pb}	Lead Activity Coefficient, γ_{Pb}
0.100	0.00465	0.0465	0.884	0.982
0.152	0.00779	0.0513		
0.200	0.0140	0.0702	0.732	0.915
0.300	0.0341	0.113	0.537	0.767
0.399	0.0727	0.182	0.355	0.592
0.499	0.185	0.370	0.168	0.337
0.603	0.304	0.504	0.0900	0.225
0.700	0.483	0.690	0.0381	0.127
0.800	0.681	0.852	0.0130	0.0651
0.900	0.904	1.00	0.00270	0.0270

from the transpiration experiments is 16.6 ± 0.6 torr; from the total pressure measurements it is 16.6 ± 0.3 torr. Lead activities calculated from the transpiration data on the basis of $p^\circ_{Pb} = 0.15$ torr [Hultgren *et al.* (*6*)] are 0.527, 0.694, and 0.794 for compositions of 0.3, 0.2, and 0.1 atom fraction sodium. These values may be compared with the values listed in Table III, which are 0.537, 0.732, and 0.884, respectively. Considering that the values in Table III were obtained by a Gibbs-Duhem integration, the agreement is good.

DISCUSSION

In relating our data with other experimental studies of the Na-Pb system, we found, in addition to Hultgren *et al.*'s compilation (*6*), Porter and Feinleib's (*8*) and Chudakov and Morachevskii's (*2*) work to be directly comparable with ours. Porter and Feinleib measured the emf of cells $Na/Na^-/Na$ in Pb up to 827° C and then extrapolated their derived activities up to 1040° C. In general, their results for activity are 30 to 40% higher than ours. It appears possible that the sampling of the cathode alloy in their cells for sodium analyses may have been faulty. Their procedure was to drill out the top portion of the product alloy and then use a smaller drill to get turnings for analyses from the remaining alloy. During the cooling of the melt (before any drilling) it is likely that various solid phases precipitated, depending on over-all composition, and that the final solidified slug was heterogeneous. Drilling out and discarding the upper portion would bias the composition of the samples taken from the lower portion. Also, the lower portion itself is likely to be heterogeneous, so random drillings taken from it also would not be representative of the composition of the melt at the operating temperature of the cell. Our disagreement with this work, then, is understandable.

Another emf study, by Chudakov and Morachevskii (*2*), covered the composition range from 0.157 to 0.572 atom fraction sodium in the temperature range 700° to 1100° K. Their measurement at 0.499 atom fraction sodium corresponds exactly in composition to ours, and extrapolation of their data to 1126° K gives a sodium activity of 0.176, in good agreement (5% discrepancy) with our value of 0.185. Also, their data for 0.157 and 0.405 atom fraction sodium can be extrapolated to 1126° K and corrected for composition (by interpolation) so that they may be compared with our results for 0.152 and 0.399 atom fraction sodium. If adjusted in this way, their values for these compositions are, respectively, 0.0086 and 0.073 for the activity of sodium; our values are 0.00779 and 0.0727. The former is in fair agreement (9% discrepancy) and the latter is in excellent agreement (no discrepancy) with the Russian scientists' results. Their results deviate from ours in both directions, and there is not enough detail in their article to assess the discrepancies further.

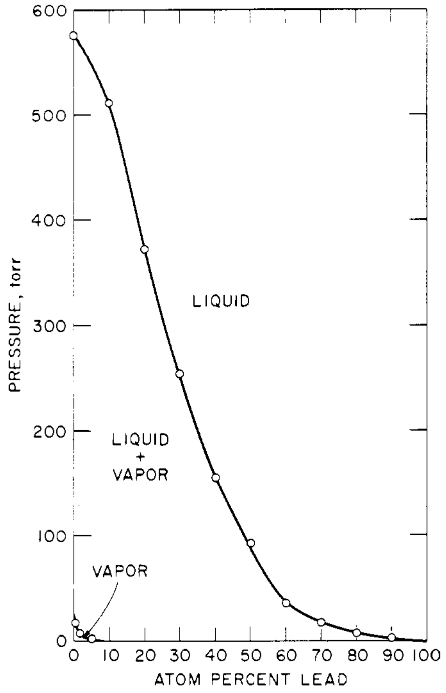

Figure 1. Pressure-composition diagram for liquid-vapor equilibria in Na-Pb system at 1126° K

In our earlier paper on the Na-Bi system, the data were correlated on the basis of a quasi-ideal solution model that involved a limited number (four) of species. The success of the treatment, though never claimed to demonstrate the existence of the invoked species, was felt to be at least suggestive in regard to species and had the positive virtue of being a useful interpolation and extrapolation technique for engineering design purposes. Despite the apparent reasonableness, however, the treatment leaves the impression of *ad libitum* selection and adjustment of parameters to cover the observations. In this respect, the situation in regard to the Na-Pb system reported here is perhaps even more susceptible to uncertainty in the setting up of a quasi-ideal solution treatment.

When this work was presented orally in 1967, the phase diagram of the Na-Pb system (*5*) showed five solid phase compounds: $NaPb_3$, NaPb, Na_9Pb_4, Na_5Pb_2, and $Na_{15}Pb_4$. In the oral presentation, the three sodium-rich compounds were treated as a single, representative, "average" compound, Na_3Pb. Since 1967, information on the additional compounds, Na_4Pb and Na_5Pb, has appeared (*7*). It would be required now that five compounds be "averaged" into one representative stoichiometry. "Na_3Pb" might still be a reasonable stand-in in this composition region, but the meaning of such a procedure is questionable. Our position on this issue is outlined in our introduction and we refrain from applying the quasi-ideal solution model. A sketch of the procedure and results for the Na-Pb system is available (*1*).

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LITERATURE CITED

(1) Argonne National Laboratory, Chemical Engineering Division, Semi-Annual Report, **ANL-7375**, 162–4 (January–June 1967).

(2) Chudakov, P., Morachevskii, A.G., *J. Appl. Chem. USSR* (English Trans) **39**, 1534 (1966).
(3) Fischer, A.K., *Rev. Sci. Instrum.* **37**, 717 (1966).
(4) Fischer, A.K., Johnson, S.A., Wood, S.E., *J. Phys. Chem.* **71**, 1465 (1967).
(5) Hansen, M., Anderko, K., "Constitution of Binary Alloys," pp. 997-1000, McGraw-Hill, New York, 1958.
(6) Hultgren, R., Orr, R.L., Anderson, P.D., Kelley, K.K., "Selected Values of Thermodynamic Properties of Metals and Alloys," p. 868, Wiley, New York, 1963.
(7) Lamprecht, G.J., Dicks, L., Crowther, P., *J. Phys. Chem.* **72**, 1439 (1968).
(8) Porter, B., Feinleib, M., *J. Electrochem. Soc.* **103**, 300 (1956).
(9) Sittig, M., "Sodium. Its Manufacture, Properties, and Uses," p. 484, Reinhold, New York, 1956.
(10) Welcher, F.J., "Analytical Uses of Ethylenediamine Tetra-acetic Acid," pp. 117, 189, Van Nostrand, Princeton, N.J., 1958.

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Melting Point Intervals of Sulfur Allotropes

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The intervals between the melting points of the four allotropes of cyclooctasulfur (designated α, β, γ, and δ) were measured by a microtechnique in sealed capillaries. New melting point values resulting from this work were β 120.14°, α 115.11°, γ 108.60°, and δ 106.0° C, all appreciably higher than currently accepted values.

AT least four allotropes of sulfur, consisting of different spatial arrangements of the ring molecule of cyclooctasulfur, S_8, and designated α, β, γ, and δ, are known to exist (*5*). The accurate determination of their melting points is of considerable importance for checking the accuracy of vapor pressure equations (*6*) and in theories describing the rates of crystal growth and the polymorphic transformations of sulfur (*2, 7*).

The currently accepted melting points (*5*) are β 119.3°, α 112.8°, and γ 106.8°. The melting point of δ-sulfur is not known.

Factors giving rise to low precision in these measurements include the following:

All the melting points are above 95.6° C and only β-sulfur is stable above this temperature. If nucleation occurs, all other forms transform rapidly to β in the region of their melting points. There is no record of δ-sulfur ever having been preserved in this temperature range and preservation of γ-sulfur in macroscopic amounts rarely occurs.

Naturally occurring sulfur is frequently contaminated with hydrocarbons, which are very difficult to remove (*1, 8*).

Liquid and gaseous sulfur contain species other than S_8 and crystals obtained from the melt or by sublimation are not initially pure cyclooctasulfur and have lowered melting points.

Sulfur crystallized from solvents is usually contaminated with solvent.

Atmospheric constituents, especially oxygen, are strongly adsorbed on sulfur.

Sufficient information is now known of the behavior of sulfur to overcome most of these difficulties. Bacon and Fanelli (*1*) and Von Wartenburg (*8*) have demonstrated methods for removing hydrocarbons, and vacuum distillation of the residue gives very pure sulfur. This can then be converted quantitatively to cyclooctasulfur by heating in an inert atmosphere for several days at about 100° (*4*).

By sealing large numbers of small crystals into fine capillary tubes and observing them on a microscope hot stage, several melting points could be observed in the same tube after appropriate thermal treatments. The intervals between these melting points could be determined with high precision. These intervals should correspond with the differences between the melting points of the various allotropes. By taking the accepted melting point of β-sulfur, the stable modification, as an internal standard, more accurate melting points for the other allotropes could be calculated. This has been done (second row of Table I). The determination of absolute melting points by any other method when using the microscope poses something of a dilemma when one comes to quote the results, because all substances in microcrystalline form melt over an appreciable range of temperature. When the crystals are in contact in a vertical capilliary tube as in most macromethods, the first crystal to melt pulls all the others together by surface wetting and this is taken as the melting point. Most melting points in the literature were obtained by this method. When the crystals are all separate from each other and observed under a microscope, however, it is more logical to take the last crystal to melt as representing the true melting point. The difference between these two types of measurement can be appreciable and for the sake of consistency no "final" melting points are given in this paper. The values given in the third row of Table I are "first" melting points. Although the hot-stage thermometer was checked only at the boiling point and ice point of water and calibrated with the standard substances quoted, measurements

Table I. Derived Melting Points of Sulfur Allotropes

Premise	M.P. β	M.P. α	M.P. γ	M.P. δ
Currently accepted	119.3	112.8	106.8	
Assuming current β MP correct	119.3	(114.3)[a]	(107.8)[a]	(105.2)[a]
Assuming mean measured β MP correct	120.14	115.11	108.60	106.0

[a] Values in parenthesis obtained by subtracting measured temperature intervals from "accepted" melting point of β-sulfur.