enthalpy differences in this region. Therefore, the differences in activity coefficients must be attributed to the change in intermolecular forces, resulting from changes in molecular structure.

Figure 3 shows the heats of vaporization-composition relationship for the three-carbon alcohol-water systems. The heat of vaporization for the various alcohol solutions shows only slight deviation with molecular structure. Thus, the intermolecular forces appear to be of less significance with respect to this parameter than in solution behavior.

Therefore, the influence of molecular structure of components in a binary system is reflected primarily in the properties of the liquid phase through changes in intermolecular forces.

ACKNOWLEDGMENT

The support of the National Science Foundation through its Grant 14297 is appreciated.

NOMENCLATURE

H_i = molar enthalpy of pure component i
$\bar{H}_i$ = partial molar enthalpy of component i
P_i = vapor pressure of pure component i
R = gas constant
T = °Kelvin
γ = activity coefficient
π = total pressure
x_i = mole fraction component i in liquid phase
y_i = mole fraction component i in vapor phase

LITERATURE CITED

(1) Bloom, C.H., Clump, C.W., Koeckert, A.H., *Ind. Eng. Chem.* **53**, 829 (1961).
(2) Brunjes, A.S., Bogart, M.J.P., *Ibid.*, **35**, 255 (1943).
(3) Gadwa, T.W., Ch.E. thesis, Mass. Inst. of Tech., Cambridge, Mass., 1936.
(4) Hands, C.H.G., Norman, W.S., *Trans. Inst. Chem. Engr. (London)* **23**, 76 (1945).
(5) Harper, W.G., Moore, J.C., *Ind. Eng. Chem.* **49**, 411 (1957).
(6) Katayama, T., *Kagaku Kogaku* **26**, 361 (1962).
(7) Kolthoff, I.M., Elving, P.J., "Treatise on Analytical Chemistry," Part II, Vol. **1**, p. 86, Interscience Publishers, New York, 1961.
(8) Plewes, A.C., Jardine, D.A., Butler, R.M., *Can. J. Technol.* **32**, 133 (1954).
(9) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(10) Shell Chemical, "Allyl Alcohol," New York, 1946.

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Constitution Diagram for the PbTe–Sb System

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The constitution diagram of the quasi-binary system PbTe-Sb has been determined by thermal analysis, metallographic, and x-ray procedures. A eutectic is formed at 89.5 ± 0.1 wt. % Sb and 601.0° C. The solid solubility of Sb in PbTe is less than 0.1 wt. % and that of PbTe in Sb is less than 0.5%.

EXPLORATORY STUDIES of the ternary system tellurium antimony-lead, by x-ray analysis and microscopic examination, revealed that the PbTe phase and antimony probably formed a true quasi-binary section. This isopleth was investigated by thermal analysis, x-ray, and microscopic examination.

EXPERIMENTAL

Materials. The lead, tellurium (American Smelting and Refining Co.), and the antimony (Bunker Hill Co.) each had a purity of 99.99+% by spectrographic analysis.

Procedure. All alloys were prepared by weighing the desired amount of each element on an analytical balance in a quartz tube, which was then evacuated, sealed off, and placed in a muffle furnace controlled at a temperature at least 50° above the melting point of the composition under study. During the 20 to 30 minutes that the alloy was held at temperature, it was vigorously shaken to ensure homogenization. The alloy weights used varied between 40 and 80 grams each, depending on the specific gravity of the alloy. After being cooled in air, the alloys were transferred to mullite (aluminum silicate) crucibles to take the thermal data.

Heating and cooling curves were recorded with the alloys under a protective atmosphere of nitrogen as the temperature was changed at a controlled rate of 2 to 4° C. per minute by a motorized variable transformer. During each cooling run, the molten alloy was stirred by a mullite rod rotated at constant speed by a Cenco variable-speed stirrer until the freezing metal stopped the motion. The temperature of the alloys was measured with a calibrated chromel-alumel thermocouple, which was protected from the molten liquid and centered in the alloy by a thin-walled mullite tube. Since the electromotive force produced by the chromel-alumel thermocouple was often greater than the range of the Honeywell Extended Range Recorder used for charting the e.m.f., an external precision potentiometer was used as an auxiliary. Critical points were checked with a Leeds and Northrup K-2 precision potentiometer.

The samples for metallographic examination were polished by conventional techniques. Etching was carried

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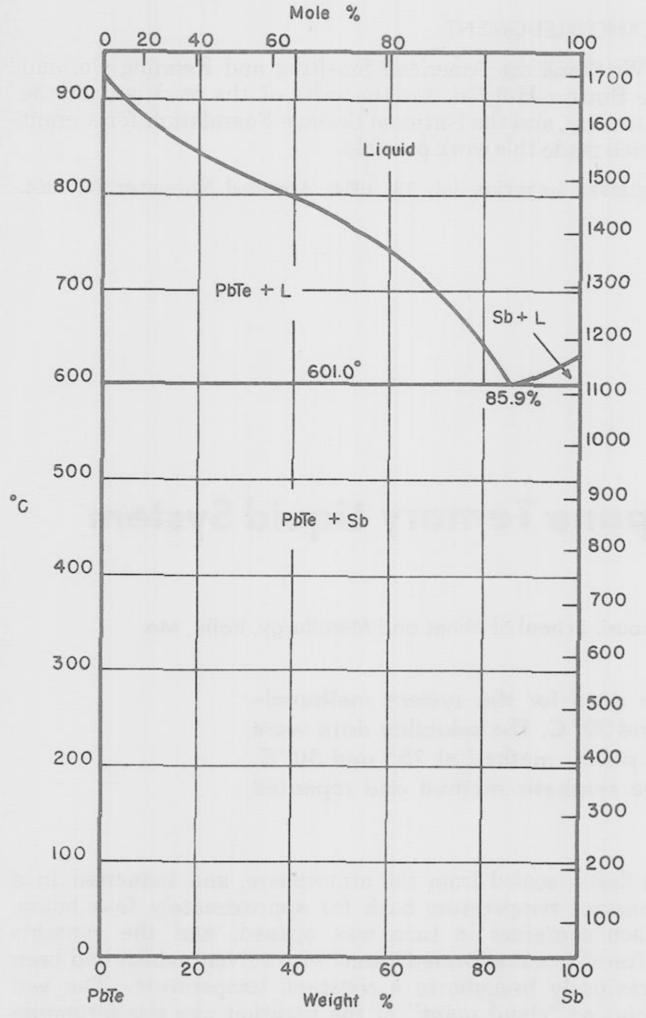

Figure 1. Constitution diagram of the PbTe–Sb system

out with a dichromate solution containing 2 grams of $K_2Cr_2O_7$, 1 gram of NaCl, 8 ml. of H_2SO_4, and 100 ml. of water.

The solid solubility limits were investigated by metallographic and x-ray techniques on alloys which had been homogenized at 590° C. X-ray diffraction patterns were taken in a 57.3 mm. Debye-Scherrer camera with nickel-filtered copper radiation at 30 KVP and 10 ma. at exposure times of 1½ to 3 hours.

Table I. Thermal Data for PbTe–Sb System

Wt. %, Sb	*Mole %, Sb*	*Liquidus, ° C.*	*Solidus, ° C.*
0.00	0.00	924.0	. . .
2.50	6.59	906.5	587.0
5.00	12.64	906.3	595.3
7.50	18.23	859.3	599.5
10.00	23.40	872.8	600.0
15.00	32.67	856.6	598.8
20.00	40.74	843.5	599.8
25.00	47.82	831.0	599.3
30.00	54.10	819.0	600.5
35.00	59.69	808.0	600.3
40.00	64.70	797.8	600.8
45.00	69.23	785.5	600.8
50.00	73.33	772.0	601.0
55.00	77.07	757.5	600.0
60.00	80.49	741.2	601.4
65.00	83.63	722.0	601.0
70.00	86.52	700.3	601.0
75.00	89.19	675.0	601.0
78.00	90.70	658.3	601.0
80.00	91.67	643.0	601.2
81.00	92.14	637.0	601.4
82.00	92.61	645.5	601.2
83.00	93.07	620.4	601.6
84.00	93.52	612.8	601.2
85.29	*94.10*	*600.8*	*601.6*
87.00	94.85	601.8	601.6
87.50	95.06	602.0	601.6
88.00	95.28	602.5	599.3
88.80	95.62	604.0	599.3
89.80	96.03	606.3	600.8
90.82	96.46	608.5	600.8
92.85	97.28	614.8	600.8
94.16	97.79	617.0	601.0
98.00	99.26	625.8	600.0
100.00	100.00	631.5	. . .

RESULTS

Thirty-five alloys were examined by thermal analysis, and 16 alloys were inspected metallographically. Table I lists the thermal data, and Figure 1 shows the phase diagram obtained. The system is a simple eutectiferous type exhibiting complete liquid solubility of the lead telluride and antimony and extremely limited solubility between the two solids. The PbTe–Sb pair forms a eutectic at 85.9 ± 0.1 wt. % (94.4 mole %) Sb and a temperature of 601.0° C. The eutectic composition was located by the intersection of the liquidus lines and by examination under the microscope of a series of alloys in the eutectic compositional-area which varied by 0.1% Sb. These were examined for the disappearance of the primary phase, approaching from both

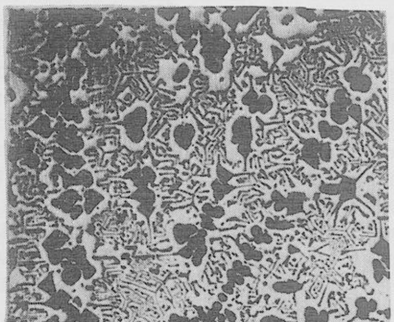

Figure 2. Microstructure of alloy containing 80% Sb and 20% PbTe, air cooled. Primary PbTe (black) and eutectic. Etchant: dichromate X75

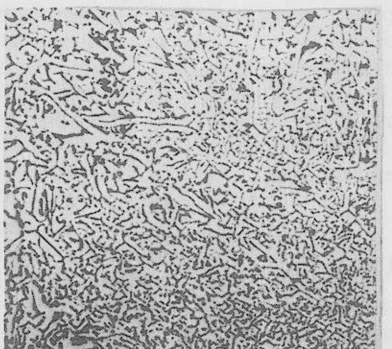

Figure 3. Microstructure of eutectic alloy: 85.9% Sb, 14.1% PbTe, furnace cooled. Etchant: dichromate X75

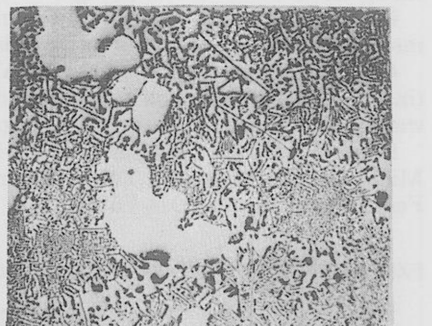

Figure 4. Microstructure of alloy containing 87.5% Sb and 12.5% PbTe, air cooled. Primary Sb (white) and eutectic. Etchant: dichromate X75

sides. Figures 2, 3, and 4 illustrate the different etching characteristics of the primary PbTe and Sb. Figure 2 is a photomicrograph of an alloy which contains primary PbTe and eutectic; Figure 3 is of the eutectic composition, and Figure 4 shows primary Sb and eutectic.

The solid solubility of Sb in PbTe is less than 0.1 wt. % and the solubility of PbTe in Sb is less than 0.5%.

ACKNOWLEDGMENT

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Equilibria and Solubility Data for the Methanol–Water–1-Nitropropane Ternary Liquid System

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The ternary-liquid solubility and equilibria data for the system methanol–water–1-nitropropane are reported at 25° and 30° C. The solubility data were determined by a modification of the "cloud point" method at 25° and 30° C. The equilibria data were determined by the synthetic method and repeated at 25° C.

DURING A STUDY of methods to calculate ternary equilibria data from the salient properties of the binaries, a need for data on a particular liquid system arose. Thus, the ternary-liquid solubility data for the methanol–water–1-nitropropane system were experimentally determined at 25° and 30° C., and the equilibria data for the same system were determined at 25° C. For this liquid system, methanol was the solute, water the solvent, and 1-nitropropane the carrier.

EXPERIMENTAL METHODS

The following standard experimental techniques and apparatus were used:

Reagents. The methanol was distilled and a heart cut with a boiling range of ±0.1° C. was taken. The water was triple distilled. The 1-nitropropane, 99% purity by weight, was obtained from Commercial Solvents Corp.

Specific Gravity. Specific gravity determinations were made with a 25-ml. Weld-type specific gravity bottle.

Refractive Index. A Bausch and Lomb dipping refractometer was used to obtain refractive index readings.

Constant Temperature Control. An Aloe precision circulating temperature control, range 15° to 100° C., ±0.01° C., was used to maintain the constant temperature bath.

Buret. Titrations were performed with a 10-ml. Kimble Micro (Class A) buret. The buret met requirements of Federal Specification DD-V581A.

EXPERIMENTAL DETERMINATION OF SOLUBILITY DATA

The solubility data were determined by a modification of the "cloud point" method which is described in detail by Othmer (*4*) and Hand (*2*). To determine the solvent lean portion of the mutual solubility curve, 20-ml. mixtures of carrier and solute were made at 10 wt. % increments from pure carrier to pure solute. These mixtures were placed in flasks, sealed from the atmosphere, and immersed in a constant temperature bath for approximately four hours. Each container in turn was opened, and the contents titrated from calibrated burets with solvent which had been previously brought to a constant temperature. The end point or "cloud point" of the titration was the formation of turbidity in the mixture. The solvent-rich portion of the solubility curve was obtained by reversing the procedure. That is, prepared samples of solvent and solute were titrated with carrier until the turbidity was observed.

Titration at Constant Temperatures. During the "cloud point" titrations, Hand and Othmer removed their samples from the constant temperature bath. The procedure described herein was modified to eliminate any effects of the ambient temperature and the heat of mixing on the mutual solubility. These possible errors were eliminated, as the vessel containing the mixture being titrated was continually agitated in the constant temperature bath during titration. This was accomplished by using a glass-bottomed, constant temperature bath, thus allowing the end point of the titration to be observed, while keeping the sample in the bath and at a constant temperature.

Agitation Time. A problem arose concerning the proper agitation time after the titration of the two-phase mixture with the third component. An erroneous cloud point results from this type of titration, unless the mixture is agitated in the constant temperature bath for 10 to 15 minutes after each titration. This was accomplished by connecting the capped flask containing the three-component mixture to the shaft of a variable speed laboratory mixer. The flask was then immersed in the constant temperature bath, while the agitation motor was supported by a ring stand.

Titration Near the Plait Point. In the concentration range of 25 to 30 wt. % water, the cloud point was indistinguishable. The situation occurred because this region is near the plait point where one phase cannot be distinguished from another.

The results of these determinations were expressed as wt. % of the three components. Refer to Table I and Figure 1.

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