the specific bond between the solute and solvent atoms, the interactions between solvent atoms which are disrupted or altered by the addition of an H atom and those between solvent atoms near the solute atom.

The $\gamma_H{}^\circ$ value calculated by the Blander model (7.8×10^3 atm$^{1/2}/X_H$ at 400 °C assuming that the fraction of the total interactions of Li or Pb atom influenced by an H atom is equal to 0.25) is consistent with the experimental results in this study (4.4×10^3 atm$^{1/2}/X_H$ at 400 °C). This value of $\gamma_H{}^\circ$ is sufficiently high to suggest a remarkable weakening of the bonds between the Li and Pb atoms near the hydrogen atom because of the setting of the preferred Li-H bonds.

Then the deviation from the ideal behavior in this system can be attributed to the onset of attractive forces between atoms absorbed in interstitial contiguous sites: these strengths are born in order to minimize the disturbance caused by the solute atom on the bonds between the alloy atoms and also on the short-range order existing in the molten state.

Concerning this, we wish to point out that in the Wu work (*14*) reported for the tritium/$Li_{17}Pb_{83}$ system, the values of $P_{T_2}{}^{1/2}/X_T$ decrease considerably when the tritium concentration increases in the alloy. This agrees perfectly with what we obtained for the H/$Li_{17}Pb_{83}$ system.

On the grounds of the hypothesis advanced a qualitative interpretation of the effect produced by the temperature on the global behavior of the system is also possible. The very small variation in the activity coefficient at infinite dilution of hydrogen in the alloy with increase of temperature could be due to the compensation of two opposite effects: the increase both in the activity coefficients of the two metallic components in the binary Li/Pb system (*1*) (the interactions that have to be partially reduced would then be minor) and in $\gamma_H{}^\circ$ in the binary H/Li system (*7*) (the interactions which can form would weaker themselves too). With a more elevated concentration of hydrogen, the differing of hydrogen activity coefficient values at the three temperatures examined (Figure 2) can be considered to be due to a minor deviation from ideal behavior at higher temperature when the interactions among solvent alloy atoms are minor.

Registry No. H_2, 1333-74-0; $Li_{17}Pb_{83}$ alloy, 73369-65-0.

Literature Cited

(1) Saboungi, M. L.; Marr, J.; Blander, M. *J. Chem. Phys.* **1978**, *68*, 1375–84.
(2) Becker, W.; Schwitzgebel, G.; Ruppersberg, H. *Z. Metallkd.* **1981**, *72*, 186–90.
(3) Ruppersberg, H.; Egger, H. *J. Chem. Phys.* **1975**, *63*, 4095–102.
(4) Ruppersberg, H.; Speicher, W. *Z. Naturforsch. A* **1976**, *31*, 47–52.
(5) Biggio, M.; Casini, G.; Farfalletti Casali, F.; Pierini, G.; Ponti, C.; Rieger, M. "Abstracts of Papers", 12th Symposium on Fusion Tecnology, Jülich, Sept 1982; Commission of the European Communities; B14.
(6) Sze, D. K.; Clemmer, R.; Cheng, E. T. "Thermal and Mechanical Design of WITAMIR blanket", proceedings presented at the 4th ANS Topical Meeting on the Technology of Controlled Nuclear Fusion, King of Prussia, PA, Oct 14–17, 1980.
(7) Veleckis, E.; Van Deventer, E. H.; Blander, M. *J. Phys. Chem.* **1974**, *78*, 1933–40.
(8) Katsuta, M.; Ishigari, T.; Furukawa, M. *Nucle. Technol.* **1977**, *32*, 297–303.
(9) Veleckis, E. *J. Phys. Chem.* **1977**, *81*, 526–31.
(10) Ihle, H. R.; Wu, C. H. In "Proceedings of the 2nd International Congress on Hydrogen in Metals, Paris, France, June 1977"; Pergamon Press: New York, 1977; Vol. 1.
(11) Hofmann, W.; Maatsch, J. *Z. Metallkd.* **1956**, *47*, 89–95.
(12) Erdmann Jesmitzer, F.; Van Pethegen, A. P.; De Wilde, R. *Metall (Berlin)* **1974**, *28*, 449–55.
(13) Sze, D. K. "Proceedings of Engineering Problems of Fusion, Chicago, IL, Oct 1981"; Institute of Electrical and Electronics Engineers: New York, 1981; pp 1213–5.
(14) Wu, C. H.; Blair, A. J. "Abstracts of Papers", 12th Symposium on Fusion Technology, Jülich, Sept 1982; Commission of the European Communities: B27.
(15) Wu, C. H. *J. Nucl. Mater.* **1983**, *114*, 30–3.
(16) Veleckis, E. *J. Less-Common Met.* **1973**, *73*, 49–60.
(17) Wagner, C. *Acta Metall.* **1973**, *21*, 1297–303.
(18) Lapidus, L. "Digital Computational for Chemical Engineers"; Peters, M. S., Ed.; McGraw-Hill: New York, 1962; Chapter 7.
(19) Blander, M. *J. Chem. Phys.* **1961**, *34*, 432–48.
(20) Alcock, C. B.; Richardson, F. D. *Acta Metall.* **1958**, *6*, 385–95.
(21) Alcock, C. B.; Richardson, F. D. *Acta Metall.* **1960**, *8*, 882–7.
(22) Mathieu, J. C.; Durand, F.; Bonnier, E. *J. Chim. Phys. Phys.-Chim. Biol.* **1965**, *62*, 1289–96.
(23) Lupis, C. H. P.; Elliott, J. F. *Acta Metall.* **1976**, *14*, 1019–28.
(24) Lupis, C. H. P.; E-Hsin Foo. *Acta Metall.* **1973**, *21*, 1409–30.
(25) Jacob, K. T.; Alcock, C. B. *Acta Metall.* **1972**, *20*, 221–32.
(26) Chiang, T.; Chang, Y. A. *Metall. Trans. B* **1976**, *7B*, 453–66.
(27) Blander, M.; Saboungi, M. L.; Cerisier, P. *Metall. Trans. B* **1979**, *10B*, 613–22.
(28) Gokcen, N. A. *Scr. Metall.* **1969**, *3*, 157–60.

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Some Thermodynamic Properties of Mellitic Acid

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The molar octanol–water partition coefficient of mellitic acid (benzenehexacarboxylic acid) at 22 °C is 0.036 if the mellitic acid dimerizes in the octanol phase with a constant of about 100 M^{-1}. The osmotic behavior of mellitic acid is independent of temperature between the freezing point and 25 °C and shows that the compound behaves much like a 1–1 electrolyte in aqueous solution, at concentrations between 0.01 and 1 *m*.

As part of a program to study the organic solvent–water partition coefficients of a series of diverse organic compounds, I have collected several thermodynamic data on mellitic acid (benzenehexacarboxylic acid).

This compound can be derived by oxidation of graphite; the aluminum salt occurs in oxidized coal humic acids as mellite $[Al_2C_6(COO)_6 \cdot 18H_2O$ (*1*)], an example of one of the relatively rare organometallic minerals (*2*).

Table I. Octanol–Water Partition Coefficient, K_{ow}, for Mellitic Acid (MA) at 22 °C

M_o, mol dm^{-3}	M_w, mol dm^{-3}	log K_{ow}	log $K_{ow}{}^a$	log $K_{ow}{}^b$
0.0001_1	0.008	−1.9 ± 0.1	−1.08	-1.08^c
0.0018	0.073	−1.61 ± 0.05	−1.29	−1.40
0.014	0.34_2	−1.39 ± 0.05	−1.24	−1.49
0.038	0.55_0 (0.51 *m*)	−1.16 ± 0.05	−1.04	−1.44
				av = −1.45 ± 0.03

[a] Value after allowing for dissociation in the aqueous phase; $k_{i,1} = 10^{-1.40}$. [b] Value after also allowing for association in octanol phase according to reaction $2MA \rightarrow (MA)_2$, $k_a = 100\ M^{-1}$. [c] Value ignored in final average.

Table II. Freezing Point Depressions of Aqueous Mellitic Acid

m, mol kg^{-1}	θ, mK	ϕ^a	m, mol kg^{-1}	θ, mK	ϕ^a
0.000 30	1.5	1.34	0.004 30	20.1	1.26
0.000 46	2.7	1.57	0.010 65	45.5	1.148
0.000 64	3.4	1.43	0.026 07	101.8	1.050
0.001 78	9.3	1.40	0.046 56	169.3	0.976
0.002 64	12.9	1.31			

[a] Osmotic coefficient defined as $\phi = -55.5(\ln a_w)/\nu m$, where $\nu = 2$.

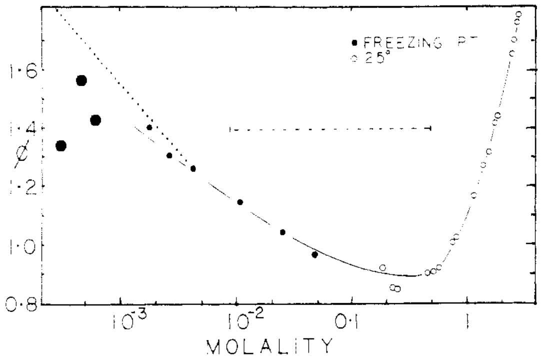

Figure 1. Osmotic coefficient for mellitic acid in aqueous solution. The sizes of the symbols indicate the imprecision. The dashed line corresponds to the concentration range over which the partition coefficients were measured. The dotted line is the theoretical osmotic coefficient corrected for dissociation.

Experimental Section

Mellitic acid from K and K Laboratories, Plainview, NY, was recrystallized from water and methanol and was 99% pure by titration with standard potassium hydroxide to the third acid dissociation (*3*).

Partitioning experiments were made at room temperature (22 ± 1 °C) and both phases were analyzed, the water phase directly by titration, and the 1-octanol phase by back-extraction into water and subsequent titration. The results are given in Table I with concentrations expressed as molarities; each value is the mean of at least two measurements at each concentration. The freezing point measurements and the isopiestic vapor pressure measurements at 25 °C were made by using techniques which have previously been described (*4*). The results are given in Tables II and III and Figure 1, with concentrations in this case expressed as molalities.

Results and Discussion

The partition coefficients given in Table I were determined in a concentration range in which the activity coefficients of electrolytes do not change by more than about 20% (*5*); nevertheless, the K values in the third column vary by a factor of 5.

The first ionization constant of mellitic acid in water is $10^{-1.40}$ (*3*); correcting the partition coefficients for this dissociation gave values for log K_{ow} ranging from −1.04 to −1.29, about a factor of 2 (see Table I). Correcting for the second dissociation had no effect at these concentrations.

Carboxylic acids are known to dimerize in organic solvents (*6*). By introduction of a dimerization constant in the octanol of about 10^2 into the data, it was possible to reduce the scatter of the three highest concentration results to good internal consistency if the low concentration value (which was the least reliable) was discarded. This hardly consitutes proof of dimerization; other evidence might confirm or deny such a conjecture.

Table III. Osmotic Coefficients of Aqueous Mellitic Acid (MA) at 25 °C

m(NaCl), mol kg^{-1}	ϕ(NaCl)^a	m(MA), mol kg^{-1}	ϕ(MA)
0.1796	0.9257	0.1807	0.9201
0.1880	0.9252	0.2035	0.8547
0.2256	0.9237	0.2444	0.8526
0.4477	0.9202	0.4551	0.9052
0.5057	0.9210	0.5113	0.9109
0.5706	0.9225	0.5675	0.9275
0.8527	0.9305	0.7796	1.018
0.9307	0.9331	0.8342	1.041
1.3919	0.9511	1.1350	1.166
1.8257	0.9738	1.3918	1.277
2.0344	0.9850	1.5189	1.319
2.4545	1.010	1.7450	1.421
2.5730	1.018	1.8180	1.440
3.6700	1.092	2.4154	1.659
4.1295	1.125	2.6651	1.743
4.2075	1.131	2.7040	1.760
4.397	1.148	2.817^b	1.792

[a] Reference osmotic coefficients taken from Gibbard et al. (*7*). [b] Saturated solution, 49.1 wt %.

The osmotic coefficients calculated from the freezing points and vapor pressures are given in Tables II and III and plotted in Figure 1. It was arbitrarily assumed that the mellitic acid released only one proton in solution, making $\nu = 2$, for purposes of calculating ϕ. At very low concentrations, the higher dissociations are important. In the case of multiple dissociation, and hence variable ν, such as exists for mellitic acid, no standard procedure applies to selecting ν; a continuously variable value might help, but other complications are then introduced in calculating activity coefficients (*5*). If the second and third ionizations of mellitic acid ($k_{i,1,2} = 10^{-2.19}$ and $10^{-3.31}$, respectively) are considered, the effective ν increases to 3.1 at 10^{-3} m and therefore increases the ϕ plotted in Figure 1 above its theoretical limiting value of 1. The corrected osmotic coefficient shown in the figure would have the value indicated by the dotted line. The freezing point values and the isopiestic values lay on a smooth continuous curve, indicating a small partial molal enthalpy for this compound in water. The sharp increase in ϕ at about 1 m is undoubtedly due to solute hydration (*5*). No attempt was made to calculate activity coefficients from the results in Tables II and III, as these would realistically require several changes of the value chosen for ν over the concentration range studied. As has been pointed out for the case of sulfuric acid, for which ν can be 2 or 3 (*5*), this creates difficulties in transforming osmotic coefficients to activity coefficients.

Acknowledgment

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Glossary

K_{ow}	partition coefficient, or molarity of solute in octanol, M_o, divided by molarity, M_w, in water in equilibrium with octanol
$k_{i,n}$	ionization constant for mellitic acid in water
k_a	dimerization constant in octanol
θ	aqueous freezing point depression, mK
ϕ	molal osmotic coefficient defined as $-1000(\ln a_s)/(\nu m W_s)$, where a_s is the solvent activity, m is the solute molality, W_s is the solvent molecular weight, and ν is chosen as 2

Registry No. Mellitic acid, 517-60-2; 1-octanol, 111-87-5.

Literature Cited

(1) Chakrabarty, S. K.; Kretschmer, H. O.; Cherwonka, S. *Soil Sci.* **1974**, *117*, 318–22.
(2) Dana, J. D.; Dana, E. S. "The System of Mineralogy"; Wiley: New York, 1944; Vol. 2, p 1104.

(3) Maxwell, W. R.; Partington, J. R. *Trans. Faraday Soc.* **1935**, *31*, 922-35.
(4) Platford, R. F. *J. Chem. Eng. Data* **1979**, *24*, 70-1.
(5) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1968.
(6) Hendrixon, W. S. *Z. Anorg. Chem.* **1897**, *13*, 73.
(7) Gibbard, J. F., Jr.; Scatchard, G.; Rousseau, R. A.; Creek, J. L. *J. Chem. Eng. Data* **1974**, *19*, 281-8.

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Coexistence Behavior of the Vapor–Liquid–Solid Equilibrium States for Argon

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Experimental measurements available in the literature for the saturated states of argon have been critically evaluated to establish the boundaries of all three coexistence regions. This treatment has permitted the description of the vapor–liquid coexistence region over the complete domain ranging from the critical point (T_c = 150.65 K, P_c = 4.886 MPa (48.02 atm), ρ_c = 529.1 kg/m^3) to the triple point (T_t = 83.79 K, P_t = 68.82 kPa (516.17 mmHg)). The vapor–solid coexistence region has been investigated from absolute zero to the triple point. For the liquid–solid coexistence region, sufficient experimental information was available to enable the development of the saturated-liquid and -solid equilibrium curves from the triple point up to 323 K (T_R = 2.15). At the triple point, this treatment yielded values for the saturated densities of 1623, 1416, and 4.117 kg/m^3 for the solid, liquid, and vapor states, respectively. All saturated equilibrium relationships have been expressed analytically and represent the boundaries for these three coexistence regions.

In order to establish the boundaries of the two-phase coexistance regions for a typical substance, argon has been selected as a test case for the following reasons. The properties of this fluid have been well studied experimentally. Because of its simple nature, this spherical monatomic molecule in its fluid state possesses only a translational degree of freedom and is devoid of rotational and vibrational contributions. Although any one of the noble gases possesses these characteristics, helium and neon of necessity are unique to themselves due to the presence of quantum effects and therefore these substances cannot be representative of general fluid behavior. Since the amount of experimental information available for krypton and xenon is limited, these two substances cannot be studied as comprehensively as argon, for which ample experimental information is presented in the literature.

The behavior of a two-phase coexistence region must satisfy the Clapeyron equation since this relationship is a rigorous thermodynamic expression relating saturation pressure to temperature as follows:

$$dP/dT = \lambda/(T\Delta v) \qquad (1)$$

where λ is the latent heat of transformation and Δv the corresponding molar volume change. If the temperature dependence of λ and Δv is known, integration of eq 1 yields the saturation pressure behavior. Generally, this information is not readily available and therefore integration of the Clapeyron equation is not usually possible without recourse to simplifying assumptions.

Table I. Critical Point Measurements Reported in the Literature for Argon

year	ref	T_c, K	P_c, MPa (atm)	ρ_c, kg/m^3
1910	Crommelin (*3*)	150.68	4.863 (47.994)	
1968	Grigor and Steele (*4*)	150.6	4.864 (48.0)	529.5
1912	Mathias et al. (*5*)			530.78
1967	McCain and Ziegler (*6*)	150.65	4.855 (47.92)	
1958	Michels et al. (*7*)[a]	150.87	4.898 (48.34)	535.91
1895	Olszewski (*8*)[a]	152.0	5.127 (50.6)	
1901	Ramsay and Travers (*9*)[a]	155.7	5.360 (52.9)	
1969	Streett and Staveley (*10*)[a]	150.9		
1968	Teague and Pings (*11*)	150.705	4.882 (48.18)	
1969	Terry et al. (*12*)	150.6		527
av		150.65	4.866 (48.02)	529.1

[a] Data excluded when averaging.

Along any path on the *PVT* surface of a single-component system, it can be shown through mathematical arguments (*1*) that the relationship between the partial derivatives is

$$(\partial P/\partial T)_s(\partial T/\partial v)_s(\partial v/\partial P)_s = 1 \qquad (2)$$

where the subscript s denotes the designated path. This path can be taken as any one of the saturation curves where the partial derivative $(\partial P/\partial T)_s$ is the slope of the saturated pressure function which is the most easily obtainable partial derivative of eq 2. Thus, if a density–temperature relationship is accessible, the slope $(\partial v/\partial P)_s$ can be determined.

Model and Data Selection

The discrimination between data represents a perennial problem that must be handled in a manner consistent with the nature of the data. Ideally, this discrimination should be independent of any analytical model in order to avoid an unintentional bias that can easily creep into the analysis. However, more often than not, this is not possible, thus necessitating the use of a model from which deviations can be calculated in order to determine the relative behavior between data sets.

The selection of data, without the involvement of a model, was possible for the screening of vapor pressure measurements for the vapor–liquid and vapor–solid coexistence regions. In this context, Wilsak and Thodos (*2*) take advantage of the essentially linear nature of the vapor pressure function when expressed as ln P vs. 1/T, to obtain a graphical representation of high resolution suitable for screening purposes. The selec-

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