

Figure 1.—Some rare earth compounds with the NaCl structure.

$N_{1-x}O_x$ is argued by comparing the lattice parameters of EuO (5.1439 \AA) and EuN (5.014 \AA). The europium ion in EuO is divalent, and in EuN it is trivalent.

If these two compounds formed a simple solid solution, $EuN_{1-x}O_x$, one would expect (from Vegard's law) that, as the composition is changed from EuN to EuO , the lattice parameter would increase. This is the reverse of what is found for the SmN - $SmN_{1-x}O_x$ system; therefore, it is concluded that the samarium ions remain in the trivalent state as oxygen is exchanged for nitrogen.

Since samarium and gadolinium are known to form continuous-phase oxynitrides in which the substitution of oxygen for nitrogen decreases the nitride lattice parameter, it is natural to ask whether this is common for the other rare earths. There are probably exceptions to this, as EuN is thought to be, since EuO has a larger lattice parameter than EuN . Another exception might be YbN since ytterbium is more like europium than are any of the other rare earths. Although there are possible exceptions to the phenomenon, the exchange of oxygen for part of the nitrogen in rare earth nitrides to form a ternary phase may explain the questionable existence of LaO , NdO (see Figure 1), and YO , although no lattice parameter has been published for YO . This exchange may also explain the existence of YO . This exchange may also explain the existence of YO . This exchange may also explain the existence of YO . This exchange may also explain the existence of YO .

Acknowledgments.—The authors are grateful to B. G. Hyde and J. O. Sawyer for many helpful discussions which were definite contributions to this work.

CONTRIBUTION FROM THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA, AND THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO 87544

Solute-Solvent Interactions in Liquid Alloys from Cadmium Vapor Pressures over Dilute Solutions of Lead in Cadmium^{1,2}

BY HAROLD S. SWOFFORD, JR.,³ AND GUY R. B. ELLIOTT

Received April 13, 1967

Lead-cadmium solutions containing 0.004–0.032 mole fraction of lead have been studied at 777°K using an isopiestic balance. The measured cadmium vapor pressures over solutions in the composition range 0.004–0.01 mole fraction of lead may be described with a deviation not greater than 0.00015 activity unit (0.2 g-cal in the cadmium partial molal free energy) by the linear relationship $P_{Cd \text{ alloyed}}/P_{Cd \text{ pure}} = 1 - 1.63N_{Pb}$, where P is the pressure over the alloy or over pure cadmium at the same temperature and N_{Pb} is the mole fraction of lead in solution. At larger concentrations curvature becomes observable, and from 0.015 to 0.032 mole fraction of lead the relationship $P_{Cd \text{ alloyed}}/P_{Cd \text{ pure}} = 1 - 2.04N_{Pb} + 33.0N_{Pb}^2$ is obeyed within 0.00034 activity unit, the cadmium activity becoming positive to Raoult's law at 0.9683 mole fraction of cadmium. This solvent behavior is tentatively interpreted as resulting from solute-solvent interactions which form complex species analogous in many respects to normal solvation reactions.

Vapor pressure measurements on some liquid metal solutions have demonstrated an unexpected complexity. Although the work was undertaken to test dilute so-

lution theory, the complexity appears to be of considerable structural interest. This paper reports the lead-cadmium solution results; references to other published work are given in the Discussion section.

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract H-73.

(3) Visiting Staff Member, Los Alamos Scientific Laboratory. Please send mail regarding this paper to Los Alamos.

TABLE I
 THE ACTIVITY OF CADMIUM ALLOYED WITH LEAD

Point no.	Balance shift, g	Cadmium mole fraction ^a	Temp, °K				ΔT , °K ^c	Cadmium activity ^d	Dev of calcn ^e
			Alloy ^b	Cadmium ^b	Alloy crossarm ^b	Cadmium crossarm ^b			
1	0.2870	0.99608	772.5	772.1	782.7	782.8	0.307	0.99368	+0.00007
2	0.7521	0.99583	773.1	772.8	783.1	783.2	0.333	0.99317	-0.00003
3	2.0044	0.99498	775.2	774.7	785.0	784.9	0.403	0.99177	-0.00015
4	3.6495	0.99311	777.6	777.1	787.4	787.4	0.555	0.98877	0.00000
5	4.7157	0.99093	778.7	778.0	789.0	788.9	0.732	0.98525	+0.00003
6	0.4478	0.99159	776.8	776.1	788.1	788.1	0.675	0.98633	+0.00004
7	1.0623	0.99073	776.5	775.7	786.3	786.5	0.751	0.98479	-0.00010
8	1.7701	0.98951	776.3	775.4	786.1	786.5	0.842	0.98294	+0.00004
9	2.2800	0.98841	776.6	775.7	787.2	787.5	0.928	0.98123	
10	2.3391	0.98827	776.5	775.5	787.2	787.2	0.943	0.98092	
11	3.2500	0.98552	777.1	775.9	787.5	787.6	1.126	0.97730	-0.00024
12	2.2654	0.98845	776.9	776.0	787.4	787.8	0.923	0.98135	
13	3.7963	0.98315	776.8	775.5	787.4	787.6	1.242	0.97496	+0.00003
14	4.3238	0.97999	777.0	775.6	787.7	787.7	1.374	0.97235	-0.00004
15	4.9036	0.97479	777.0	775.5	787.5	787.5	1.516	0.96954	0.00000
16	5.3810	0.96793	777.4	775.8	789.5	789.6	1.586	0.96817	-0.00034
17	3.4335	0.98480	777.4	776.3	789.5	789.6	1.171	0.97642	-0.00020

^a Points 1-5: initial cadmium, 1.32191 g; lead, 0.00923 g; 6.09201-g balance shift = 1.00000-g cadmium shift. Points 6-17: initial cadmium, 1.15525 g; lead, 0.01693 g; 6.12800-g balance shift = 1.00000-g cadmium shift. ^b Measured with a Pt-10% Rh thermocouple against an ice junction to the nearest 0.1°K. ^c Measured with a Pt-Pt-10% Rh thermocouple to 0.005°K temperature difference between the alloy and the pure cadmium, but the average value of the approaches from the different composition directions is carried to 0.001°K for calculation purposes. ΔT was calculated, as earlier,⁶ from millivolts using a bias correction for each run as follows: points 1-5 reduced by 0.0029 mV; points 6-17 reduced by 0.0037 mV. The bias was established by finding that constant correction necessary for each run to make the data extrapolate linearly to unit activity at pure solvent. ^d The vapor activity is relative to that over pure liquid cadmium using an equation consistent with Hultgren, namely, $P_{Cd}^0 = \exp[-(13,119/T) + 19.950 - 1.05676 \ln T]$; R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963. ^e Calculated using equations in the text.

Experimental Information

The isopiestic balance as described in detail elsewhere⁴⁻⁶ provides a precise means to measure composition and thermodynamic activity simultaneously. In this case measurements were made using volatile cadmium and effectively nonvolatile lead. A reservoir of pure cadmium at some temperature was allowed to vaporize or condense cadmium so that a lead-cadmium alloy at slightly higher temperature could alter its composition and reach pressure equilibrium with the reservoir cadmium. From published data the vapor pressure is known as a function of temperature. The temperature difference between the alloy and the reservoir when pressure-composition equilibrium has been achieved is thus a measure of the vapor activity over an alloy at that composition and temperature.

The lead was 99.98% Pb by the manufacturer's report and by Los Alamos Scientific Laboratory spectroscopic analysis. Its density was checked and found proper. The only further purification of this lead was to cut off surface contamination and to examine by microscope for iron chips from the cutters on the sample pieces. Cadmium (99.999% pure by manufacturer's report) was vaporized into the isopiestic balance tube as discussed elsewhere.⁶

The present lead-cadmium data were taken by the "double reversal" technique⁶ using a newly built balance⁷ mounted in its own frame and made in a somewhat different shape although of generally similar internal design. Instead of a Leeds and Northrup Wenner potentiometer, a somewhat less sensitive Leeds and Northrup K-3 potentiometer had to be used for these measurements.

Results

Table I indicates the results, which are plotted in Figure 1 as mole fraction of cadmium vs. cadmium

(4) G. R. B. Elliott and J. F. Lemons, *J. Phys. Chem.*, **64**, 137 (1960).

(5) G. R. B. Elliott and J. F. Lemons in "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 153.

(6) G. R. B. Elliott, J. F. Lemons, and H. S. Swofford, Jr., *J. Phys. Chem.*, **69**, 933 (1965).

(7) We wish to acknowledge the contribution of Dr. P. C. Nordine, who nearly completed the construction of this balance while he was carrying out measurements with other balances already in operation.

activity, *i.e.*, the vapor pressure of the alloy divided by the vapor pressure of pure cadmium at the same temperature. Activity is used because it is the thermodynamic quantity most closely related to the accurately measured temperature difference between the alloy and the cadmium reservoir and, further, because it is little affected by small changes in the alloy temperature. The point numbers indicate the order in which the measurements were made, points 1-5 representing measurements with the first balance tube while the remaining points were made with a second tube.

These results may be described analytically by two equations except for a narrow transition region. The first equation

$$\frac{P_{Cd \text{ in soln}}}{P_{Cd \text{ pure}}} = 1 - 1.63N_{Pb \text{ in soln}} \quad (1)$$

applies in the range 0.004-0.010 mole fraction of lead. Near 0.012 mole fraction of lead the transition region is observed. For the range 0.015-0.032 mole fraction of lead the data may be described by the equation

$$\frac{P_{Cd \text{ in soln}}}{P_{Cd \text{ pure}}} = 1 - 2.04N_{Pb \text{ in soln}} + 33.0N_{Pb \text{ in soln}}^2 \quad (2)$$

This is shown in the Dundee plot in Figure 2 where the data are presented as $(1 - a_{Cd})/N_{Pb}$ vs. N_{Pb} . Both equations give straight lines on this plot with the coefficient of the N_{Pb}^2 term established by the slope of the line and the coefficient of the N_{Pb} term found from the extrapolated intercept. Deviations from these equations are listed in Table I.

Discussion

Previous discussion⁶ of the absolute and relative accuracy of the isopiestic balance applies here. The establishment of an isothermal isopiestic equilibrium

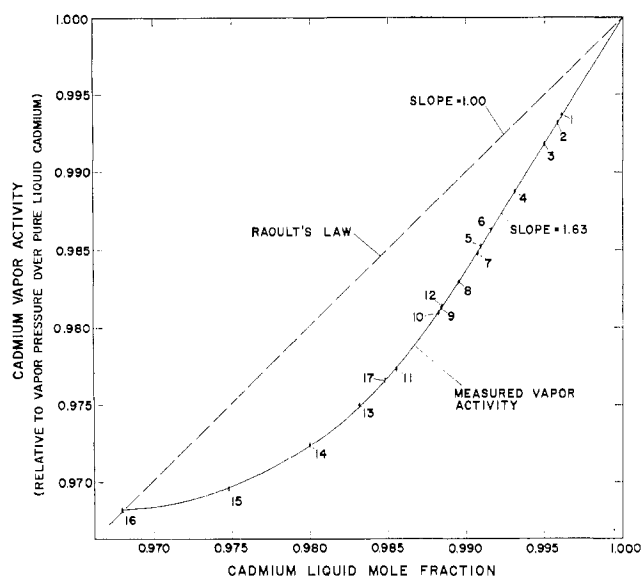


Figure 1.—The activity of cadmium containing small amounts of lead.

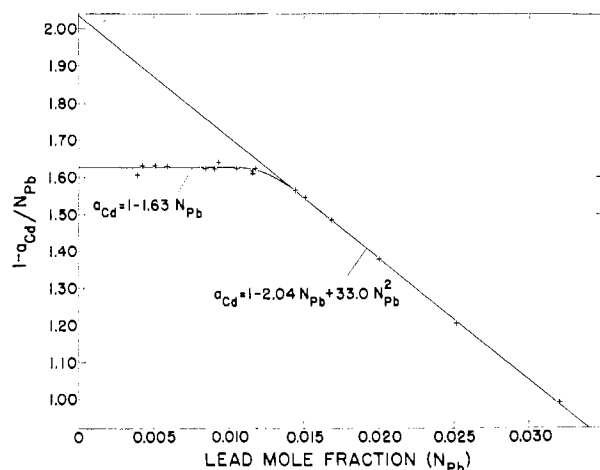


Figure 2.—Dundee plot to show the fit of the data to the equation form used.

is quite independent of gas complexity, and the establishment of the present equilibrium is essentially independent of gas complexity; the calculation of activity, however, does involve the assumptions that gaseous cadmium is monatomic and $P_{Cd}/P_{Cd \text{ pure}} = f_{Cd}/f_{Cd \text{ pure}}$. The fugacity assumption has been treated,⁶ but polyatomic cadmium or cadmium-lead gas molecules have not been directly discussed.

Polyatomic cadmium molecules seem to be ruled out as an important contribution to the gas phase (a) by the entropy of vaporization of pure cadmium⁸ which has a normal value over a range of temperatures, and (b) by the absence of Cd polymers in mass spectrograph studies.⁹ It should be noted, as well, that gas complexity could account for complexity in only

one system—the interpretation of the Pb-Cd behavior as an effect of gas complexity would require the corollary conclusion of solution complexity not otherwise in evidence for all systems whose activity-mole fraction relationships now appear to pass smoothly through that activity region in which the Pb-Cd solution appears to show a change of behavior.

If significant but as yet unidentified gaseous molecules containing lead (*e.g.*, $PbCd(g)$) were present, these results could not be reproducible when the solution was returned to a composition measured earlier. Thus the fact that point 17 falls on line between points 11 and 13 argues against this possibility.

Other liquid alloys have also shown changes in behavior somewhat like those indicated for the lead-cadmium solutions at 0.012 mole fraction of lead, and such changes have been demonstrated by several techniques. Examples: Au-Cd solutions have shown abrupt changes of slope in activity-mole fraction relationships by emf¹⁰ and vapor pressure,¹¹ and electrical resistivity effects¹¹ can be correlated with vapor pressure behavior in the latter work. Au-Sn solutions¹² as studied by emf show abrupt slope changes, and relatively rapid slope changes are shown by vapor pressure studies of Sn-Hg¹³ and Au-Hg¹⁴ solutions. On the other hand, precise measurements of other metallic solutions show simple relationships over considerable ranges of composition; these latter results indicate that the complex behavior is probably associated with the systems measured rather than due to a peculiarity of the measuring techniques. Simple behavior is shown for Ga-Cd,⁶ Ni-Cd,¹⁵ Ag-Cd,¹⁴ and Ag-Hg¹⁴ by vapor pressure and for Cu-Sn¹² and Ag-Sn¹² by emf.

This kind of complex behavior could be explained in terms of a type of solvation, *i.e.*, the creation of interaction units¹¹ through the bonding of solute atoms to their solvent neighbors with a change in these interaction units at 0.012 mole fraction of lead. This type of interaction involving more or less discrete entities in solution might be amenable to treatment by some chemical bond theory, such as a modified ligand field theory, rather than the usual band theory which considers the solution as a whole. We are unable to handle such a treatment and would appreciate work others would choose to do in this area.

In this system the vapor pressure of cadmium does not appear to be approaching Raoult's law asymptotically as the solution becomes more dilute. Of course, it is possible that in solutions more dilute than those measured the behavior would change and Raoult's law would be approached, or, possibly, for this sys-

(10) B. L. Houseman and G. R. B. Elliott, submitted for publication.

(11) G. R. B. Elliott, C. C. Herrick, J. F. Lemons, and P. C. Nordine "Structure in Liquid Au-Cd and Ce-Cd Solutions. Vapor Pressure and Electrical Resistivity. Liquid Compounds, Two-Liquid Regions, Premonitory Phenomena, and Freezing," Los Alamos Scientific Laboratory Report LA-3526, 1966.

(12) G. R. B. Elliott and J. F. Lemons, *J. Electrochem. Soc.*, **114**, 935 (1967).

(13) D. R. Conant, submitted for publication.

(14) D. R. Conant and H. S. Swofford, Jr., submitted for publication.

(15) D. R. Conant and G. R. B. Elliott, submitted for publication.

(8) See reference given in footnote *d* of Table I.

(9) G. M. Martynovich, *Vestn. Mosk. Univ., Ser. Mat. Mekhlan. i Astron.*, No. 5, 67 (1958), as reported by An. N. Nesmeyanov, "Vapor Pressure of the Elements," translated by J. I. Carasso, Academic Press Inc., New York, N. Y., 1963.

tem the solute does not obey Henry's law so the solvent could not be expected to obey Raoult's law.

However, as presented elsewhere in detail,^{6,16-20} the authors, on the basis of reasoning from molecules,

(16) G. R. B. Elliott, J. F. Lemons, and H. S. Swofford, Jr., "An Alternative Treatment of Solvent Activity in the Raoult's Law Region. The Gallium-Cadmium System," Los Alamos Scientific Laboratory Report LA-2997, 1963.

(17) G. R. B. Elliott and J. F. Lemons, *J. Phys. Chem.*, **69**, 2185 (1965).

(18) G. R. B. Elliott, submitted for publication.

are not surprised when they find the activity of the solvent obeying an equation of the form $a_1 = 1 - k_1 N_2$ with $k_1 \neq 1$.

(19) H. S. Swofford and G. R. B. Elliott, "Further Tests of Dilute Solution Equations and Thermodynamic Relationships: The Vapor Pressure of Cadmium over Liquid Alloys Containing Small Amounts of Lead," with Appendix in Reply to O'Keeffe's Comments²⁰ by G. R. B. Elliott, H. S. Swofford, Jr., and D. R. Conant, Los Alamos Scientific Laboratory Report LA-3657, 1965.

(20) M. O'Keeffe, *J. Phys. Chem.*, **70**, 596 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO, NEW YORK 14214

Application of Extended Hückel Theory to the Calculation of the Potential Energy Curve of Diatomic Copper

By C. R. HARE, T. P. SLEIGHT, W. COOPER, AND G. A. CLARKE

Received November 9, 1967

Extended Hückel theory molecular orbital calculations using the Cusachs approximation of the exchange or resonance integrals have been carried out on the Cu_2 molecule. The agreement with the reported experimental internuclear distance, dissociation energy, and vibrational stretching frequency, which define the potential energy curve, is good. The results are also in accord with the ionization potential and the energy of the first spectral transition. Other approximations to the off-diagonal matrix elements are shown to be less satisfactory.

Introduction

The extended Hückel molecular orbital theory^{1,2} has proved to be a simple but useful approach for the description of many molecular properties. The theory requires only the appropriate choice of the Coulomb integrals or orbital energies (H_{ii}), the orbital exponents (single Slater or double ζ), and a physically reasonable method of approximating the exchange or resonance (H_{ij}) integrals. This approach has been applied, with some success, to the calculation of a limited number of properties of simple molecules such as H_2 and H_2O ^{3,4} and to the more complicated transition metal complexes² or metalloporphyrins.⁵ However, if the extended Hückel theory is to be considered of general utility, it should be capable of reproducing many of the physical observables of simple molecules. In this connection, Allen and Russell⁶ have recently carried out bond angle calculations on a number of small molecules using the extended Hückel method. Their results have shown that the extended Hückel theory is capable of reproducing both the *ab initio* Hartree-Fock solutions and the known shapes of small molecules. They also provided the theoretical justification which allows the sum of one-electron energies to represent the total molecular energy in determining molecular geometry. However, extensive

semiempirical calculations have not⁷ as yet established general criteria for the determination of the equilibrium bond distances of widely differing molecules. It is therefore only a convenience that most semiempirical calculations employ experimentally determined molecular geometries.

It seemed desirable to initiate related semiempirical calculations with a systematic examination of the consequences of some parameter choices and approximations to the off-diagonal terms for the homonuclear diatomic molecules of the transition metals. Calculations on these molecules are further simplified by the absence of charge separation which precludes the need for corrections to the energy such as the Madelung term and iterations to self-consistent charge. Recently, information on some of the physical properties of the homonuclear diatomic molecules of the transition metals has become available.⁸⁻¹² Of these molecules, gaseous diatomic copper has been the most extensively studied, information being available for the dissociation energy, equilibrium internuclear distance, vibrational frequency, ionization potential and energy of the first transition ($^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$). Enough information is therefore available to allow a meaningful investigation and test of the semiempirical extended Hückel theory on the Cu_2 molecule.

(1) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(2) F. A. Cotton, *Rev. Pure Appl. Chem.*, **16**, 175 (1966).

(3) L. C. Cusachs, *J. Chem. Phys.*, **43**, S157 (1965).

(4) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967).

(5) M. Zerner and M. Gouterman, *Inorg. Chem.*, **5**, 1699 (1966).

(6) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967).

(7) G. A. Clarke, unpublished results.

(8) D. N. Travis and R. F. Barrow, *Proc. Chem. Soc.*, 64 (1962).

(9) M. Ackerman, F. E. Stafford, and J. Drowart, *J. Chem. Phys.*, **33**, 1784 (1960).

(10) P. Schissel, *ibid.*, **26**, 1276 (1957).

(11) A. Kant, *ibid.*, **41**, 1872 (1964).

(12) A. Kant and B. Strauss, *ibid.*, **41**, 3806 (1964).