the disk along with the product if the flow of hydrogen was adjusted properly.

Since large quantities of both boron and selenium were used, and only small amounts of the product could be collected because of the size of the fritted disk, the reaction was never run to completion and a yield could not be calculated. However, when the amorphous boron was used for more than three consecutive runs the yield of boron sesquiselenide obtained as a function of time decreased sharply. Possible reasons for this decrease may have been the partial sintering of the boron into a clinker and subsequent loss of surface area.

Attempts to determine the solubility of boron sesquiselenide in various non-aqueous solvents were inconclusive because of the traces of moisture which could not be removed, but they indicated that the product was insoluble in anhydrous ether and carbon disulfide, as would be expected for an ionic species.

This reaction was considered as a means of preparing boron sesquitelluride, but it failed to proceed, probably because of the absence of sufficient quantities of hydrogen telluride in the gaseous phase since, unlike hydrogen selenide, the equilibrium concentration of the hydrogen telluride decreases as the temperature is increased.[12]

Present work is being directed toward an elucidation of the crystal structure and an investigation of some chemical properties of this molecule.

[12] L. M. Dennis and R. P. Anderson, *J. Am. Chem. Soc.*, **36**, 882 (1914).

Correspondence

Critical Temperatures of Metals and their Estimates by Gates and Thodos

Sir:

In recent papers[1–3] it was shown that the temperature range of *liquid metals*, *i.e.*, the range from the melting to the critical point, is far greater than for any other type of substance. It extends, in view of their elementary and atomic nature, far beyond the thermal limits of existence of any other solid or liquid; even the stablest of the latter dissociate into atoms at about 5000–6000°K. In contrast, the refractory metals such as Re, Ta, and W will be liquids up to a critical temperature of about 20,000, 22,000, and 23,000°K., respectively.

It also was shown[1–3] that one can construct a liquid temperature range diagram of metals demonstrating the relationship between liquid (and saturated vapor) density *vs.* temperature over the whole liquid temperature range, from the melting point to the critical point, by using the theorem of corresponding states of van der Waals, the law of rectilinear diameter of Cailletet and Mathias, and experimental data on heats and entropies of vaporization, vapor pressure, and particularly experimental liquid density data over as wide a temperature range as possible.

Subsequently it has come to our attention that Gates and Thodos[4] estimated the critical temperatures of metals, but arrived at values that differed substantially from ours, as the comparison in Table I shows.

TABLE I

COMPARISON OF THE CRITICAL TEMPERATURE OF METALS ESTIMATED BY THE METHOD OF GATES AND THODOS[4] *vs.* THE INSTITUTE'S

	Normal b.p.,[5] °K.	Critical temp., °K.	
		Gates and Thodos	R. I. T. U.
W	5800	11500	23000
Mo	5100	9880	17000
Sn	2960	5809	8700
Pb	2024	3584	5400
Na	1163	2124	2800

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[1] A. V. Grosse, "The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures," Report of the Research Institute of Temple University, September, 1960; see also *Nuclear Sci. Abstr.*, **15**, 4018, 31197 (1961).

[2] A. V. Grosse, American Rocket Society, Space Flight Report to the Nation, New York Coliseum, Oct. 9–15, 1961, Paper No. 2159-61.

[3] A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **22**, 23 (1961).

[4] D. S. Gates and G. Thodos, *A.I.Ch.E. Journal*, **6**, 50 (1960).

[5] All data on normal boiling points and ΔH_{vap} are taken from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Advances in Chemistry Series No. 18, 1956.

As one can see our critical temperatures are greater than the normal boiling points of the metals by a factor of 4 (W) to 2.5 (Na).

Gates and Thodos plotted all the known critical temperatures (T_c) of the elements *vs.* their normal boiling points (T_b) and arrived at the simple relationship

$$T_c = 1.4732\, T_b^{1.0818}\ (T \text{ in } ^\circ\text{K.})$$

This is a similar relationship to an earlier one of Meissner and Redding,[6] supposedly applicable to all elements, namely

$$T_c = 1.70\, T_b - 2.0\ (T \text{ in } ^\circ\text{K.})$$

Both of these empirical relationships, however, are based on the experimental critical temperatures of *the noble gases and non-metals only.*

From the T_c so obtained and the vapor pressure equation, Gates and Thodos extrapolated the critical pressure, P_c. Using both these critical constants, the constants a and b of the van der Waals equation of state were obtained. The critical volume $V_c = 3b$.

The relationship of Gates and Thodos and the previous one of Meissner and Redding, however, *do not apply to metals.*

The following facts have to be considered. The nature of the attractive forces in a liquid between atoms of the noble gases or the diatomic molecules of such elements as H, O, N, and all the halogens, which were used to estimate the empirical relationships, on the one hand, and the metals, on the other, are quite different. In the first case we have weak van der Waals forces and in the second much stronger metallic bonds. This is forcefully demonstrated by comparing the energy necessary to separate a gram atom of the liquid into separated atoms or molecules in the gas phase, *i.e.*, the heat of vaporization, ΔH_{vap}, for example at the normal boiling point, as shown in Table II.

The decisive piece of evidence, however, is the following one. Gates and Thodos, in their extensive literature survey on the subject, unfortunately missed the experimental determination of the critical constants of mercury, *the only metal* for which such constants are known.

TABLE II

HEATS OF VAPORIZATION, ΔH_{vap}, AT THE NORMAL BOILING POINT OF NON-METALS AND METALS, IN CAL./G.-ATOM

	Non-metals		Metals
H_2	107.9	Hg	14,137
N_2	667.5	Na	21,280
O_2	815	Zn	27,560
F_2	781	Pb	42,880
Cl_2	2439	Ag	60,690
Br_2	3585	Sn	69,400
I_2	4985	Fe	83,900
S	2300	Zr	139,000
		Mo	142,000
		W	191,000

Bender,[7,8] during World War I, measured the density of both liquid and saturated vapor of Hg up to 1380°, or 1650°K. Later, Bernhardt[9] determined the vapor pressure up to 1700°K. and finally, thirty years ago, Birch,[10] at Bridgman's laboratory at Harvard, succeeded in determining the critical temperature and pressure. By correlating all the experimental data,[1-3] which show a great (although not perfect) degree of internal consistency, the following values for the critical constants are obtained. They are compared with those obtained from Gates and Thodos' relationship.[11]

	Experimental	Gates and Thodos' relationship
T_c, °K.	1733 (±50)	1135
P_c, atm.	1587 (±50)	134
D_c, g./cm.^{3}	4.70 (±0.20)	0.99
V_c, cm.^{3}/g.-atom	42.7 (±2.0)	202.4

Thus, we see that the experimental values for Hg are off by large factors from Gates and Thodos' estimates, particularly for D_c, V_c, and P_c.

Furthermore, all the experimental evidence obtained recently at the Institute on the liquid densities of various metals, such as Pb,[12] Ag,[12] Cu,[13] Sn,[14] In,[12] Bi,[14] and Mg,[13] up to their respective normal boiling points, eliminates still further the possibility that the estimates of Gates and Thodos can be correct. One example will suffice. Our experimental[15] and extrapolated values for the

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(6) H. P. Meissner and E. M. Redding, *Ind. Eng. Chem.*, **34**, 521 (1942).

(7) J. Bender, *Physik. Zeit.*, **16**, 246 (1915).

(8) J. Bender, *ibid.*, **19**, 410 (1918).

(9) F. Bernhardt, *ibid.*, **26**, 265 (1925).

(10) F. Birch, *Phys. Rev.*, **41**, 641 (1932).

(11) Meissner and Redding's estimates are similar.

(12) *J. Inorg. & Nuclear Chem.*, in press.

(13) *J. Phys. Chem.*, in press.

(14) A. D. Kirshenbaum, Final Report, "High Temperature Inorganic Chemistry," National Science Foundation, Research Grant 15540, Research Institute of Temple University, October 31, 1961.

(15) A. D. Kirshenbaum, J. A. Cahill, and A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **22**, 33 (1961).

density of liquid and saturated vapor of lead are

	T, °K.	$D_{\text{liq}}{}^{3}$, g./cm.^{3}	$D_{\text{id. gas}}$, g./cm.^{3}
Experimental values	1600	9.361	. . .
	2024 (N.B.P.)	8.803	0.0012
Extrapolated values	2500	8.167	0.008
	3000	7.49	0.029
	3500	6.79	0.072

If Gates and Thodos' value of 3584°K. for T_c of Pb is correct, there should be a sudden change in the whole density *vs.* temperature relationship for the liquid and saturated vapor beyond the normal boiling point, in contrast to all known liquids.

The knowledge of true critical temperatures permits us to establish a very simple density *vs.* temperature relationship[1-3] for most of the liquid range of any metal and also the change in surface tension or energy *vs.* temperature for any metal.[16]

It goes without saying that it would be highly desirable to determine the critical temperature of other metals besides mercury; some of them are certainly within reach of modern high temperature experimentation.

(16) A. V. Grosse, *J. Inorg. & Nuclear Chem.*, in press.

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RECEIVED JANUARY 22, 1962

Observation of Four d-d Transitions in a Copper Chelate[1]

Sir:

We have discovered four optical transitions, in the d-d absorption region, in single crystals of bis-(3-phenylacetylacetonato)-copper

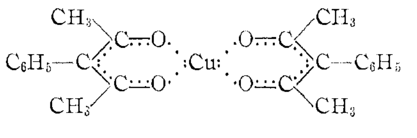

Fig. 1 and 2 show the spectra of a thin section of one face at room temperature and at liquid nitrogen temperature.

In view of the current diversity of opinion[2-5] concerning the assignments of the bands in the spectrum of the related compound, bis-(acetylacetonato)-copper, we think it worthwhile to show these preliminary results without the full analysis (which, including the necessity for a full X-ray structural determination and for observing other faces, will take us over a year to complete).

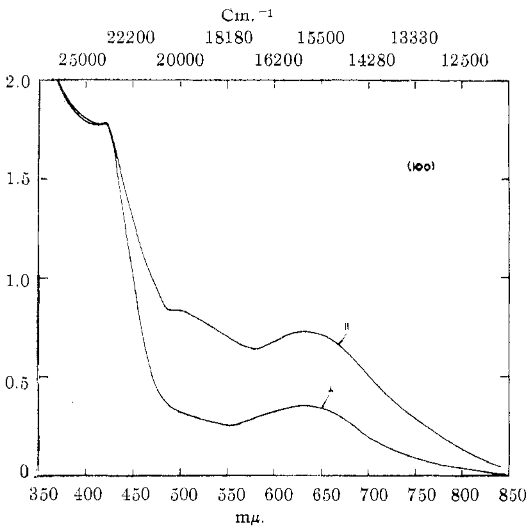

Fig. 1.—Polarized spectra of copper bis-3-phenylacetylacetonate (room temperature).

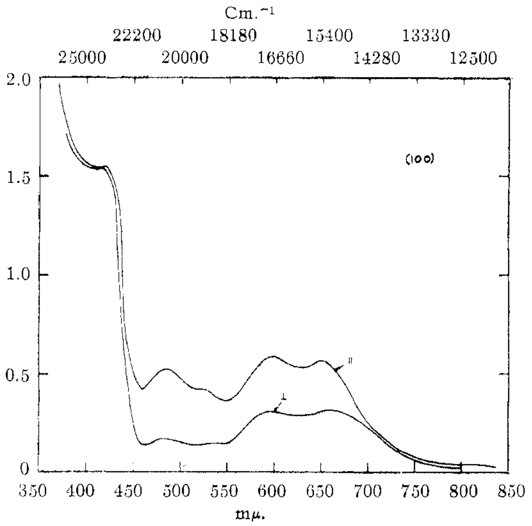

Fig. 2.—Polarized spectra of copper bis-3-phenylacetylacetonate (liquid nitrogen temperature).

It is noteworthy that in addition to the four bands of comparable intensity in the visible, there is a stronger fifth band at slightly higher energy. This fifth band we have ascribed to a ligand transi-

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(1) This work is supported by the National Science Foundation and by an Alfred P. Sloan Foundation Research Fellowship awarded to R. L. Belford.

(2) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5** (1962); R. L. Belford and T. S. Piper, *ibid.*, **5** (1962), both in press.

(3) J. Ferguson, *J. Chem. Phys.*, **34**, 609 (1961).

(4) D. P. Graddon, *J. Inorg. & Nuclear Chem.*, **14**, 161 (1960).

(5) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).