# Thermochemistry of the Liquid System Lead(II) Oxide–Boron Oxide at 800°

BY J. L. HOLM AND O. J. KLEPPA

Calorimetric measurements at 800° are reported for the partial enthalpies of solution of each of the two components in the binary liquid system PbO–B₂O₃. The concentration dependence of the partial enthalpies shows inflection points for oxygen to boron ratios of about 3.5–4.0 and 1.84–1.91, respectively. On the basis of the Lux–Flood acid–base theory for oxide melts, it is suggested that these inflection points reflect the formation of two complex borate anions with corresponding oxygen to boron ratios.

## Introduction

During the past few years high-temperature calorimetry has proved to be an important tool in the study of fused-salt mixtures. So far the bulk of the work in this field, both experimentally and theoretically, has been devoted to mixtures formed by relatively low-melting simple salts such as the nitrates and the halides. Less attention has been given to the study of the more complex melts formed by the combination of oxides.

As far as is known, the only calorimetric investigation in this area is that of Yokokawa and Kleppa,[1,2] who studied the heats of solutions of a number of solid oxides of divalent metals in liquid vanadium(V) oxide near 700°. At this temperature the solubility of some of these oxides is very restricted. Therefore, the reported data largely consist of the heats of solution of the considered solid oxides in nearly pure $V_2O_5$. Only for lead(II) oxide did the work of Yokokawa and Kleppa cover a significant range in composition. In this case it was found that the partial heat of solution of PbO in PbO-$V_2O_5$ mixtures varies little with composition from $N_{PbO} = 0$ to $N_{PbO} \sim 0.6$. This was interpreted to indicate that $VO_3^-$ (or its polymers) is *not* a significant species in these oxide melts.[1]

In the present work the investigation of mixed oxide melts is extended to the system PbO–$B_2O_3$. The choice of this system was based on two considerations.

(1) For some time we have used lead borate melts and lead–cadmium borate as solvents for solution calorimetry at high temperature. In this work we have found a melt of composition $3MO \cdot B_2O_3$ to be a good solvent for a variety of solid oxides of acidic, basic, and amphoteric character. For this reason we have considered it to be of particular interest to explore further the thermodynamic properties of the PbO–$B_2O_3$ system.

(2) The phase diagram for PbO–$B_2O_3$, studied in detail by Geller and Bunting,[3] shows a wide liquid region at reasonably low temperatures. At 800°, which is a convenient temperature for precise calorimetric work, the liquid region extends from about 15 mole % $B_2O_3$ to 100% $B_2O_3$. Since, at this temperature, pure

PbO is a solid while $B_2O_3$ is an exceedingly viscous liquid, the usual calorimetric approach based on a direct determination of the integral enthalpy of mixing from the two pure components was not feasible. We adopted instead an approach based on the measurement of the two partial enthalpies of solution in melts of different composition.

## Experimental Section

The chemicals used in the present work were yellow lead(II) oxide and boric acid (Baker Analyzed reagent). Anhydrous $B_2O_3$ glass was prepared from boric acid by heating this in air in a platinum dish at 1000°. When the release of water vapor had ceased, the liquid was quenched by pouring it out on a cold silver plate.

All calorimetric experiments were performed in a single-unit microcalorimeter for work up to 1100°. This calorimeter has a thermopile consisting of 54 Pt—Pt–13Rh couples connected in series. In other respects the apparatus is similar to the twin unit for work up to 800° used by Hersh and Kleppa.[4]

The liquid oxide melt, in an amount of about 25 g, was contained in a gold crucible of about 17-mm diameter and 60-mm height. The lead oxide to be dissolved was contained in a very shallow platinum cup of about 10-mm diameter. This cup was attached, by means of three platinum wires, to a fused-silica tube which could be manipulated from outside the furnace system. The solution reaction was initiated by lowering the platinum cup into the melt. Stirring was achieved by moving the cup up and down in the crucible.

The boron oxide was added to the solvent from a somewhat deeper platinum cup. In this case stirring was achieved by means of a platinum-covered silica plunger. The viscous $B_2O_3$ liquid was displaced and brought to reaction by inserting the plunger into the platinum cup.

Two calorimetric experiments were performed for each filling of the gold crucible. In the first experiment 0.3–0.5 mmole of PbO was added to the melt, while in the second measurement 1.5–3.0 mmoles of $B_2O_3$ was used. Through the first addition the mole fraction of lead oxide in the melt was increased by about 0.005; through the second addition it was decreased by about 0.02.

Calibration of the calorimeter was by the gold drop method, based on the heat content equation for pure gold given by Kelley.[5] A correction of 1% was applied for the small heat pickup of the 2-mm gold wire during its drop into the calorimeter.

## Results and Discussion

We give in Table I a summary of the experimental results obtained in the course of the present work. From this table it will be noted that our experiments

(1) T. Yokokawa and O. J. Kleppa, *Inorg. Chem.*, **3**, 954 (1964).
(2) T. Yokokawa and O. J. Kleppa, *ibid.*, **4**, 1806 (1965).
(3) R. F. Geller and E. N. Bunting, *J. Res. Natl. Bur. Std.*, **18**, 585 (1937).

(4) L. S. Hersh and O. J. Kleppa, *J. Chem. Phys.*, **42**, 1309 (1965).
(5) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 584, U. S. Government Printing Office, Washington, D. C., 1960.

Table I

Heats of Solutions at 800° of Lead Oxide and Boron Oxide
in $PbO-B_2O_3$.

| Composition of mixture, $N_{PbO}$ | Heat of solution,[a] kcal/mole | |
|---|---|---|
| | $\Delta H_{PbO(s)}/\Delta n_{PbO}$ | $\Delta H_{B_2O_3(l)}/\Delta n_{B_2O_3}$ |
| 0.83 | $+4.6 \pm 0.2$ (3) | $-19.0 \pm 0.5$ (2) |
| 0.80 | $+4.2 \pm 0.2$ (3) | $-15.4 \pm 0.5$ (3) |
| 0.75 | $+3.9 \pm 0.2$ (3) | $-12.9 \pm 0.3$ (2) |
| 0.67 | $+3.5 \pm 0.2$ (4) | $-12.3 \pm 0.3$ (3) |
| 0.60 | $+3.0 \pm 0.2$ (4) | $-11.9 \pm 0.2$ (2) |
| 0.55 | $+2.8 \pm 0.3$ (3) | $-10.6 \pm 0.2$ (2) |
| 0.50 | $+2.5 \pm 0.2$ (2) | $-9.7 \pm 0.2$ (2) |
| 0.45 | $+1.4 \pm 0.2$ (3) | $-8.2 \pm 0.2$ (3) |
| 0.40 | $-2.6 \pm 0.4$ (2) | $-5.2 \pm 0.2$ (2) |
| 0.33 | $-5.7 \pm 1.5$ (3) | $-4.0 \pm 0.2$ (2) |

[a] The quoted uncertainties represent the average deviation from the mean. The numbers in parentheses are the numbers of experiments performed.

covered the composition range from $N_{PbO} = 0.83$ to $N_{PbO} = 0.33$. For higher lead oxide contents we would have crossed the liquidus; for lower lead oxide concentrations the melt is too viscous for effective calorimetry at 800°.

The experimental quantities in Table I are $\Delta H_{PbO}/\Delta n_{PbO}$ and $\Delta H_{B_2O_3}/\Delta n_{B_2O_3}$; *i.e.*, the reported numbers represent the ratio of the observed enthalpy change to the amount of material added. In separate experiments with lead oxide we found, for a given solvent composition and within our experimental error, that these ratios were essentially independent of the magnitude of $\Delta n$ when this was changed within a factor of 3. Therefore we conclude that the ratios given in Table I to a good approximation represent the relative partial molar heat contents of the two components, $\bar{L}_{PbO(s)}$ and $\bar{L}_{B_2O_3(l)}$.

We give in Figures 1 and 2 a graphical representation of the dependence of $\bar{L}_{PbO(s)}$ and $\bar{L}_{B_2O_3(l)}$ on composition. In the case of $\bar{L}_{PbO(s)}$ this curve should extrapolate to 6.1 kcal/mole at $N_{PbO} = 1$; this is the calorimetrically determined heat of fusion of lead oxide as given by Rodigina, *et al.*[6] This value has been included in Figure 2.

In Figures 1 and 2 the two solid curves represent what we consider to be the "best" curves, based on the experimental values of $\bar{L}_{PbO}$ and $\bar{L}_{B_2O_3}$ given in Table I. These two curves should be connected through the Gibbs–Duhem relation

$$N_{PbO}d\bar{L}_{PbO} + N_{B_2O_3}d\bar{L}_{B_2O_3} = 0 \qquad (1)$$

We have tested the internal consistency of our two sets of data by means of this relation, adopting as a common reference point the values of $\bar{L}_{PbO}$ and $\bar{L}_{B_2O_3}$ at $N_{PbO} = 0.67$, which are $+3.5 \pm 0.2$ and $-12.3 \pm 0.3$ kcal/mole, respectively. By graphical integration of (1), using the trapezoidal method, we have in this way calculated the values represented by the two broken curves in Figures 1 and 2. We find, as expected, some discrepancy between the solid and broken curves as we move away from the common reference point. However, on the whole, the agreement between the two curves must be considered to be quite satisfactory.

(6) E. N. Rodigina, K. Z. Gomel'skii, and V. F. Luginina, *Russ. J. Phys. Chem.*, **35** 884 (1961).
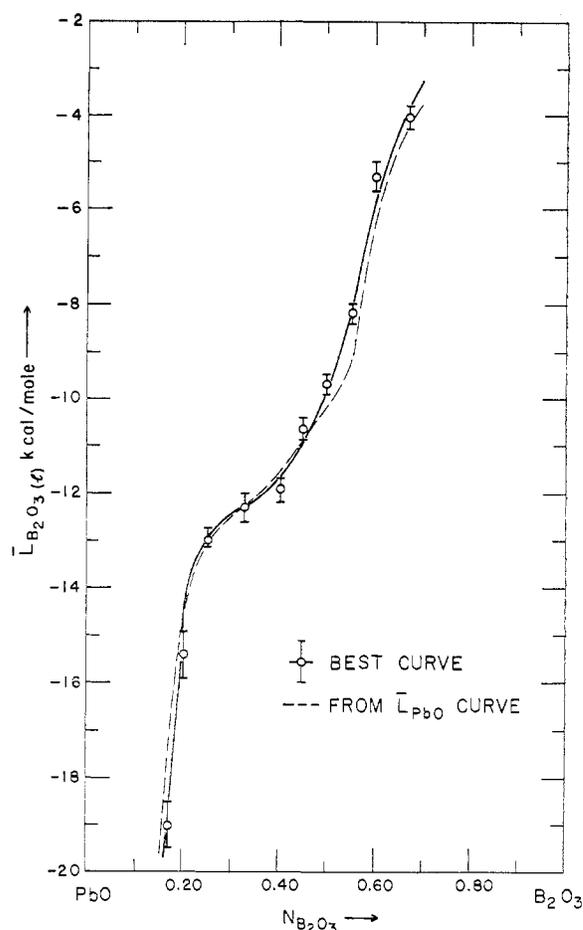


Figure 1.—Partial enthalpies of solution of liquid $B_2O_3$ in lead-borate melts at 800°.

In considering the significance of the enthalpy curves given in Figures 1 and 2, we should like to refer first to the recent calorimetric investigations of the $MgCl_2-alkCl$ mixtures by Kleppa and McCarty.[7] These authors find, for the salts of the larger alkali ions ($K^+$, $Rb^+$, $Cs^+$), that the mixtures exhibit a pronounced special stability at $N_{MgCl_2} = 0.33$. This stability presumably is related to the presence at this composition of a high proportion of the species $MgCl_4^{2-}$ which is relatively little dissociated into $Mg^{2+}$ and $4Cl^-$. It also gives rise to a sharp dependence of the partial enthalpy on composition with an inflection point at $N_{MgCl_2} = 0.33$.

For the purpose of the present discussion we should like to adopt the Lux–Flood[8,9] approach to the acid–base properties of oxide melts. In this approach the basicity of the melt is measured by the oxygen ion activity, through the equilibrium

$$\text{base} = \text{acid} + O^{2-}$$
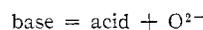
Among the two oxides considered in the present work PbO is a moderately strong base ($Pb^{2+}$ is a weak acid), while $B_2O_3$ is a strong acid. When $B_2O_3$ is dissolved in

(7) O. J. Kleppa and F. G. McCarty, *J. Phys. Chem.*, **70**, 1249 (1966).

(8) H. Lux, *Z. Elektrochem.*, **45**, 303 (1939).

(9) H. Flood and T. Førland, *Acta Chem. Scand.*, **1**, 592 (1947).
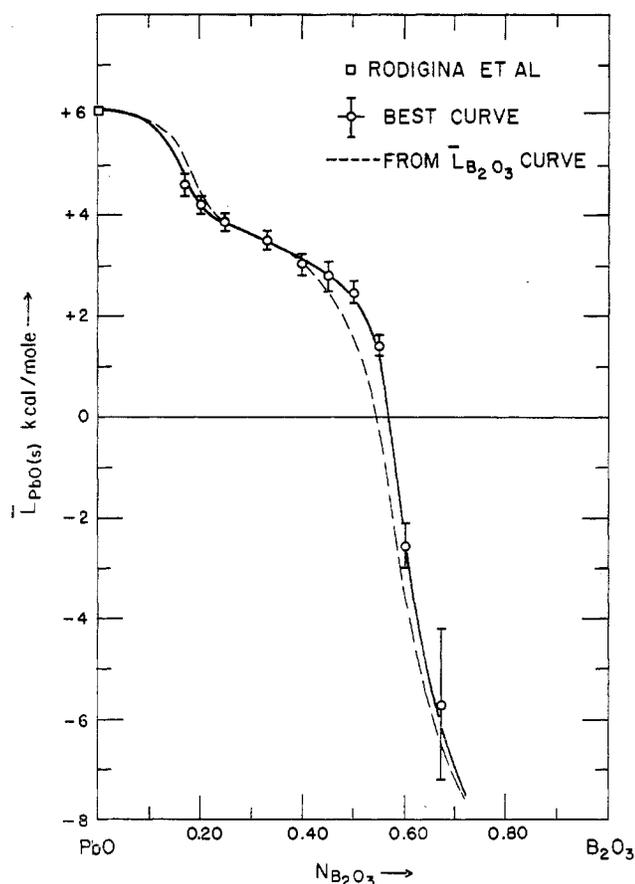
Figure 2.—Partial enthalpies of solution of solid PbO in lead–borate melts at 800°.

PbO, we accordingly anticipate a strong acid–base reaction of the type

$$\text{PbO} + \text{B}_2\text{O}_3 = \text{Pb}^{2+} + \text{borate-1 anion} \qquad (2)$$
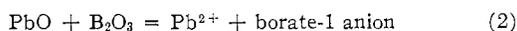
To a first approximation the heat of reaction will be a measure of the relative acid–base strength of the two oxides.

We do not know the character of the borate-1 anion which is formed as a result of this reaction. However, if we use Figures 1 and 2 as a guide, it seems likely that the sharp dependence of $\bar{L}_{\text{B}_2\text{O}_3}$ on composition in the range $N_{\text{B}_2\text{O}_3} = 0.16$–$0.20$ must be attributed to this anion. In this interpretation Figures 1 and 2 may be considered to represent "titration curves," with the "equivalence point" for the first step in the titration of PbO with B$_2$O$_3$ occurring near $N_{\text{B}_2\text{O}_3} = 0.16$–$0.20$.

From the curves in Figures 1 and 2 it may be inferred that borate-1 should have a ratio of oxygen atoms to boron atoms of between 4:1 and 3.5:1. While our calorimetric data do not permit us to draw any definite conclusions regarding the actual structure of this anion, one may guess at entities such as BO$_4$$^{5-}$ or B$_2$O$_7$$^{8-}$ which are analogous to SiO$_4$$^{4-}$ and Si$_2$O$_7$$^{6-}$. In any event, our results clearly suggest that this borate anion must be one in which a very high fraction of the boron atoms are four-coordinated with respect to oxygen. This appears to be at variance with the conclusions reached by Leventhal and Bray[10,11] in their recent nmr studies

of glasses in the high lead oxide region of the system PbO–B$_2$O$_3$. For a glass of composition 4PbO·B$_2$O$_3$ these authors conclude that only about 13 ± 4% of the boron atoms are four-coordinated with respect to oxygen.

From the appearance of the curves in Figures 1 and 2 between $N_{\text{B}_2\text{O}_3} = 0.25$ and $N_{\text{B}_2\text{O}_3} = 0.50$ it is indicated that in this range the partial heats change to only a moderate extent; *i.e.*, the acidity changes relatively little with composition. In this region the melt has *buffer* character and presumably will contain an increasing amount of a second borate anion (borate-2 anion) as $N_{\text{B}_2\text{O}_3}$ increases. It is worth noting that this buffer character of the melt is consistent with our earlier observation that a melt with mole fraction $N_{\text{B}_2\text{O}_3} = 0.25$ is a good solvent both for acidic and basic oxides.

The sharp dependence of the partial heats on composition in the range $N_{\text{B}_2\text{O}_3} = 0.55$–$0.60$ marks the end of the buffer region and suggests that the oxygen to boron ratio in the borate-2 anion falls somewhere in the range 1.84–1.91. This ratio is intermediate between that of the simple metaborate ion (BO$_2$$^-$, ratio 2.0) and the tetraborate ion (B$_4$O$_7$$^{2-}$, ratio 1.75). Our results indicate that the borate-2 anion differs from these two ions and from their polymers. To some extent this is supported by the appearance of the PbO–B$_2$O$_3$ phase diagram, which shows no maximum at the composition corresponding to BO$_2$$^-$ and a very flat maximum only in the vicinity of the compound PbB$_4$O$_7$. Therefore B$_4$O$_7$$^{2-}$ clearly must be highly dissociated in the liquid state.

On the other hand, in view of the oxygen to boron ratio for the borate-2 anion indicated by our results, one may well speculate about the existence of an anion such as B$_8$O$_{15}$$^{6-}$ or [B$_4$O$_7$–O–O$_7$B$_4$]$^{6-}$. However, at the present time this must remain speculation.

For mole fractions of B$_2$O$_3$ higher than 0.67 the borate melt is highly viscous at 800°. This accounts in part for the large error associated with our determination of the partial heat of PbO in a melt of $N_{\text{B}_2\text{O}_3} = 0.67$. From the phase diagram work of Geller and Bunting[3] it is known that in the high B$_2$O$_3$ range the PbO–B$_2$O$_3$ system has a miscibility gap which closes at $N_{\text{B}_2\text{O}_3} \sim 0.90$ and 785°. An extrapolation of our values for $\bar{L}_{\text{B}_2\text{O}_3}$ beyond $N_{\text{B}_2\text{O}_3} = 0.67$ suggests that $\bar{L}_{\text{B}_2\text{O}_3}$ may indeed become positive before it finally goes to zero at $N_{\text{B}_2\text{O}_3} = 1$. Such a behavior might be expected from the existence of the miscibility gap.

Finally, it should be mentioned that an emf study of the liquid system PbO–B$_2$O$_3$ at 1000° has been reported by the Russian workers Lepinskikh and Esin.[12] This study, which involved the use of a formation cell of the type Pb(l) | PbO–B$_2$O$_3$ | Pt,O$_2$, gives information on the excess partial free energies of PbO(l) over wide ranges in composition. Unfortunately these free energy data and our own enthalpies refer to two different temperatures. Nevertheless, a rough comparison is possible and

(10) P. J. Bray, M. Leventhal, and H. O. Hopper, *Phys. Chem. Glasses*, **4**, 47 (1963).

(11) M. Leventhal and P. J. Bray, *ibid.*, **6**, 113 (1965).

(12) B. M. Lepinskikh and O. A. Esin, *Russ. J. Inorg. Chem.*, **6**, 625 (1961).

suggests that the partial excess entropies for PbO(l) in this system have quite large negative values. Presumably these negative entropies must be related to the increased order created in these mixtures through the formation of the complex borate anions. It would be of considerable interest to pursue this problem further by the study of other highly complex-forming mixtures such as, *e.g.*, $PbO-SiO_2$. For this system free energy data have been reported by Richardson and Webb.[13] A calorimetric investigation has been initiated.

(13) F. D. Richardson and L. E. Webb, *Bull. Inst. Mining Met.*, **584**, 529 (1955).

# The Photochemistry of Borazine. Preparation of B-Monohydroxyborazine, Diborazinyl Ether, and B-Monoaminoborazine[1]

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Products of the photochemical reactions of low-pressure mixtures of borazine and oxygen and borazine and water vapor have been identified by mass and infrared spectra as $B_3N_3H_5OH$ (B-monohydroxyborazine) and $(B_3N_3H_5)_2O$ (diborazinyl ether). The ether derivative is the more stable compound and can be isolated in small quantities. The product of the photochemical reaction of borazine with ammonia is identified as $B_3N_3H_5NH_2$ (B-monoaminoborazine).

## Introduction

Borazine chemistry has developed greatly in the past few years. One area of borazine chemistry that has not been explored extensively is photochemistry. Little work has been reported on the reactions of borazine that are photosensitized by a second reagent or which require absorption of light by the borazine molecule. It has been shown that borazine does absorb ultraviolet light in four diffuse bands starting at about 1995 A and extending into the vacuum region.[2] In this paper we describe results that illustrate the potential advantages of photochemical pathways for the synthesis of borazine derivatives. The systems selected for study are borazine–oxygen, borazine–water vapor, and borazine–ammonia.

## Experimental Section

The reaction vessel was constructed from a round-bottom 2-l. Pyrex flask fitted with two side arms as shown in Figure 1. A double-wall quartz immersion well capable of transmitting light down to 1800 A was set into a standard taper joint at the neck of the flask. The volume between the outer walls of the immersion well was evacuated prior to the start of the experiment. The light source was a Hanovia medium-pressure Hg lamp, which provides an intense region of radiation around 1850 A. To maintain the vessel at room temperature, the lamp was cooled by circulating precooled nitrogen through the immersion well. The reaction vessel was joined on one side to a series of four cold traps and on the other side directly to the vacuum pumps. The reaction products were pumped through the cold traps starting at −35° and continuing to −45, −80, and −196°. These traps were cooled in slush baths of 1,2-dichloroethane–Dry Ice, chloro-

benzene–Dry Ice, acetone–Dry Ice, and liquid nitrogen, respectively. The products in each trap were analyzed mass spectrometrically. Infrared spectra of products with low volatility were obtained by means of solid films in a low-temperature infrared cell. This cell was assembled from a 9-cm Pyrex infrared cell fitted with a standard taper joint for insertion of a copper jacket to accommodate a 0.5-in. KBr window. The jacket and window were cooled by thermal conduction from an internal cold reservoir containing liquid nitrogen. The window assembly could be rotated from the position used for deposition of a sample from one of the traps to a position of alignment with the optical path. Spectra were obtained with Perkin-Elmer Model 337 grating spectrophotometer.

In the borazine–oxygen system the reagents were mixed in the reaction vessel by first adding borazine at the desired pressure and then adding $O_2$ from an auxiliary reservoir at an excess backing pressure. The quantity of $O_2$ added was determined from the ratio of the volumes of the reaction vessel and reservoir and the change of $O_2$ pressure in the reservoir. In separate experiments the total pressures of the reactants were varied between 10 and 40 mm, while the pressure ratio of borazine to oxygen was varied between 2:1 and 1:3. The exposure times ranged from 10 min to 1 hr.

In the borazine–water system $H_2O$ was added to the reaction vessel first. Borazine was then added from a reservoir at an excess backing pressure. Since it is known that water and borazine react thermally under certain conditions,[3] the pressure of $H_2O$ was always maintained below its vapor saturation point. Experiments were conducted with reactants at a total pressure of about 13 mm and pressure ratios of borazine to water varying between 2:1 and 1:2. Borazine–ammonia mixtures initially were in a molar ratio of 7:1 at a total pressure of 16 mm. The irradiation time in all cases was 20 min.

Borazine was prepared from $LiBH_4$ and $NH_4Cl$.[4] An impurity, $B_2H_5NH_2$, noted from its infrared spectrum, was removed as a

(1) Work supported by the Army Research Office (Durham) and the Advanced Research Projects Agency.
(2) J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *J. Chem. Phys.*, **15**, 598 (1947).
(3) E. Wiberg, K. Hertwig, and A. Bolz, *Z. Anorg. Chem.*, **256**, 177 (1948); see also W. E. Weibrecht, Ph.D. Thesis, Cornell University, 1964.
(4) G. W. Schaeffer, R. Schaeffer, and R. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951).