Summary

1. No exchange between radioactive cobaltous ion and hexammine cobaltic nitrate, chloropentammine cobaltic chloride, dichlorodipropylenediamine cobaltic chloride, trinitrotriammine cobalt, and chlorodinitrotriammine cobalt was found to occur within the limits of experimental error.

2. Probably the reduction of cobaltic ion by water is a more rapid reaction than the exchange reaction.

3. No exchange of cobalt atoms in cobaltous cobalticyanide was found to occur within the limits of experimental error.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Densities, Surface Tensions and Parachors of Diborane, Boron Triethyl and Boron Tribromide. The Atomic Parachor of Boron

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The suggestion made by Sugden[3] that the parachor is a measure of molecular volume at constant surface tension has been supported by Bayliss.[4] Using atomic parachor data, Bayliss was able to calculate bond radii for quadrivalent atoms and packing radii for univalent atoms which are in good agreement with the values secured by other methods. Moreover, Bayliss showed that the increase in bond radius for a quadrivalent atom, observed when its tetrachloride is converted to the tetraethyl, is paralleled by a corresponding increase in its atomic parachor. It is desirable that additional information concerning the correlation between bond radii and atomic parachors be available.

In the compounds of boron there is considerable variety in the environment of the boron atom and the bond distances in many of these compounds have been determined. In the present investigation the parachors of diborane, boron triethyl and boron tribromide have been determined. These parachors, together with those recorded in the literature for boron trifluoride, boron trichloride, methyl borate and ethyl borate, are compared with the data available on the bond distances. It is shown that a close correlation exists between the effect of bond type on the parachor and the effect on the bond radius of boron.

Experimental

Materials.—Boron trichloride and boron tribromide were made by the action of the halogens on powdered "Moissan" boron at 650°. The compounds were freed of excess halogen by allowing them to stand over mercurous chloride, and then were purified by fractional distillation.

Diborane was prepared by the reaction of boron tribromide with hydrogen, according to the method described by Stock and Sütterlin.[5] Its high purity was demonstrated by comparing its vapor tension at several temperatures with the values given by Stock and Kuss.[6]

Boron triethyl was prepared by the action of zinc diethyl on boron trichloride and was purified by fractional distillation. Its purity was demonstrated by analysis and by determination of its physical constants.

Density, Surface Tension and Parachor of Diborane.—The density of liquid diborane was determined pycnometrically at −105.1, −112.5 and −129.5°, employing a pycnometer calibrated with ethylene at the same temperatures, and using the values for the density of ethylene given by Maass and Wright.[7] The values for duplicate runs checked closely and were plotted to give a straight line corresponding to the equation

$$d = 0.3140 - 0.001296t\,°\mathrm{C}.$$

from which the density values given in Table I were calculated.

The surface tension of diborane was measured by the maximum bubble pressure method, using the cell previously described.[8] The cell was placed in a thermostat containing pentane cooled with liquid air, and the temperature was measured by an ethylene vapor pressure thermometer.[9] The surface tension cell was calibrated with ethylene, using the data for surface tension and density of ethylene given by Maass and Wright.[7]

Determinations of the surface tension of seven samples of diborane were made over the temperature range −129.5 to −108.2° and were found to agree well. These data are summarized in Table I, together with the parachor values calculated by the usual methods. The mean value found for

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[1] Present address: Standard Oil Development Co., Linden, N. J.

[2] Present address: E. I. du Pont de Nemours and Co., Newark, N. J.

[3] Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930.

[4] Bayliss, THIS JOURNAL, **59**, 444 (1937).

[5] Stock and Sütterlin, *Ber.*, **67B**, 407 (1934).

[6] Stock and Kuss, *ibid.*, **56**, 789 (1923).

[7] Maass and Wright, THIS JOURNAL, **43**, 1098 (1921).

[8] Sidgwick and Laubengayer, *ibid.*, **54**, 984 (1932).

[9] Stock, *Z. Elektrochem.*, **29**, 354 (1923).

the parachor of diborane is 121.9. The fact that the parachor does not change appreciably with change in temperature indicates that diborane undergoes no dissociation in the range studied.

TABLE I

DENSITY, SURFACE TENSION AND PARACHOR OF DIBORANE

Temp., °C.	Density	Surface tension, dynes/sq. cm.	Parachor
−129.5	0.4818	19.94	121.4
−120.3	.4698	18.32	121.9
−115.6	.4640	17.51	122.1
−112.5	.4600	16.95	122.1
−108.2	.4542	16.12	122.1

The results obtained in this investigation on the density, surface tension and parachor of diborane agree remarkably well with the data reported by Stock, Wiberg and Mäthing,[10] considering the difficulties involved in making measurements on this system.

Densities, Surface Tensions and Parachors of Boron Triethyl and Boron Tribromide.—The densities were determined pycnometrically and the surface tensions were measured by the maximum bubble pressure method. The data for 30° are listed in Table II, together with the corresponding values for the parachors.

TABLE II

DENSITIES, SURFACE TENSIONS AND PARACHORS OF BORON TRIETHYL AND BORON TRIBROMIDE AT 30°

	Density at 30°C.	Surface tension, dynes/sq. cm.	Parachor
Boron triethyl	0.6774	19.84	305.46
Boron tribromide	2.6080	27,78	220.7

Discussion

Table III summarizes the parachor and bond distance data for the seven compounds of boron. The values for the atomic parachor of boron were calculated from the molecular parachors using the atomic parachor constants suggested by Bayliss[4] for carbon, hydrogen, fluorine, chlorine and bromine, and that suggested by Mumford and Phillips[11] for oxygen. Since these atomic constants were obtained for compounds where the atom in question forms a single bond to carbon, the values for the atomic parachor of boron in Table III are on the basis of boron forming three single bonds and having a sextet of electrons in its outer shell. The observed bond distances and the sums of the single bond radii listed are taken from Pauling,[12] except for the bond distance for methyl borate.[13] The bond distance for ethyl borate has not been determined. The sums of the single bond radii give the bond distances to be expected when boron forms three single bonds and has a sextet of electrons. Comparison of the atomic parachor values for boron with the differences between the observed bond distances and the sums of the single bond radii shows that, in all but one case, small observed bond distances are accompanied by small parachors.

In the planar boron triethyl molecules the boron has a sextet of electrons in its outer shell, forming three single bonds to carbon. The observed B–C distance may be assumed to be equal to the sum of the single bond radii of carbon and boron. The value 19.86 obtained for the atomic parachor of boron is, therefore, that of tricovalent boron with a sextet of electrons.

The values for the atomic parachor of boron in boron trifluoride, boron trichloride, boron tribromide, methyl borate and ethyl borate are all lower than that for boron triethyl, and the observed bond distances are lower than the sum of the single bond radii. In all these cases the small bond distances may be accounted for by postulating carbonate-like resonance,[12] giving the boron an octet of electrons and increasing its covalence to four. The low parachor values for boron reflect the decrease in molecular volume accompanying the double bonding. The abnormally small B–F bond distance is associated with an abnormally low parachor.

The double bonding assumed in these boron compounds involves, in addition to the formation of three normal covalent bonds, the donation of an electron pair to boron to give a fourth bond, and the boron becomes more negative. The coördination number of boron is three, as in boron triethyl. Sugden[3] found that formation of such a "semi-polar double bond" was associated with decrease of several parachor units; this is in harmony with the data for the boron compounds. This type of double bonding should not be confused with the case of double bonding in the unsaturated organic compounds, where the setting up of a double bond involves equal contribution of electrons by both atoms involved, and where the coördination number of carbon is less than that for

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(10) Stock, Wiberg and Mäthing, *Ber.*, **69**, 2811 (1936). The work on diborane reported in the present paper is taken from a thesis presented to the Faculty of the Graduate School of Cornell University by R. P. Ferguson in partial fulfillment for the degree of Doctor of Philosophy, June, 1935.

(11) Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

(12) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(13) Private communication from S. H. Bauer on unpublished work.

TABLE III

Compd.	Parachor obsd.	Atomic parachor of boron	Obsd. bond distance	Sum of single bond radii	Type of bonding
$B(C_2H_5)_3$	305.46	19.86	B–C 1.56[d]	1.56	Three single bonds: Boron has sextet of electrons
BF_3	87.3[a]	8.1	B–F 1.30	1.43	Carbonate-like resonance Boron has octet of electrons
BCl_3	178.8[b]	15.0	B–Cl 1.74	1.78	
BBr_3	220.7	15.2	B–Br 1.87	1.93	
$B(OCH_3)_3$	243.7[c]	17.8	B–O 1.38	1.45	
$B(OC_2H_5)_3$	363.1[c]	17.5		1.45	
B_2H_6	121.9	14.7	B–B 1.86	1.58	Resonance of two electron, one electron and no electron bonds
			B–H 1.27	1.09	Boron with seven electrons

[a] Wiberg and Mäthing, ref. 15. [b] Mills and Robinson, *J. Chem. Soc.*, 1823 (1927). [c] Etridge and Sugden, *ibid.*, 989 (1928). [d] The value for B–C was obtained from boron trimethyl.

single-bonded carbon. Here, although the double bond distance is considerably less than the single bond distance, there is a parachor increment probably due to decrease in coördination number.

The atomic parachor for boron in diborane is small, whereas the observed bond distances are larger than the sum of the single bond radii. The larger bond distances have been shown[14] to be those expected if the structure involving resonance between two-electron bonds, one-electron bonds, and no bonds is assumed. The small value for the atomic parachor may be understood if one remembers that it was calculated by using the increment for hydrogen bonded by a pair of shared electrons, that is, as if there were two independent BH_3 molecules rather than one B_2H_6 molecule. The combination of these two BH_3 groups would involve interpenetration, giving a decrease in molecular volume and therefore a lower value for the parachor. At the same time the B–H bond distances increase because these bonds now consist of something less than two electrons, but the increase in molecular volume and parachor due to this is more than offset by the effect of interpenetration of the BH_3 groups.

Stock, Wiberg and Mäthing[10] concluded from the parachor of diborane that it has an ionic structure. This conclusion does not seem to be well advised. The unusual constitution of diborane makes it impossible to decide what atomic and structural parachor constants should be used for calculating the parachor. Since bond type has such a large effect on parachor, and since this effect is not known with precision, the wide use of parachor measurements to determine molecular configurations is unsound.

The parachor of boron trifluoride mono-diethyl etherate has been reported[15] to be equal to the sum of the molecular parachors of boron trifluoride and ethyl ether. This fits in very nicely with the postulated double bond–single bond resonance structure for the trifluoride. Instead of the fluorine atoms donating a pair of electrons to give boron an octet, the oxygen of the ether acts as donor. It is to be noted that here the change in coördination number is not accompanied by a change in parachor. The bond distances in the etherate are not known.

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Summary

1. The densities, surface tensions and parachors of diborane, boron triethyl and boron tribromide have been determined.

2. The variation of the atomic parachor of boron with change in bond type has been compared to the deviations of observed bond distances from the single bond distances.

3. The change of environment of boron has been shown to be accompanied by a change in parachor which, qualitatively, is that to be expected from the change in bond radius. This supports the suggestion that the parachor has the dimensions of volume.

4. The fact that the parachor of diborane is small while the bond distances are larger than the single bond values is shown to be reasonable.

5. The large variation of observed parachor with change in bond type makes the use of parachor measurements for determination of molecular structure unsound in many cases.

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(14) Bauer, THIS JOURNAL, **59**, 1096 (1937).

(15) Wiberg and Mäthing, *Ber.*, **70**, 690 (1937).