sulfur and condensed, with the aid of liquid air, in a second tube, C, which was then sealed off at K. After opening valves B and D, the contents of C were swept by nitrogen through lead oxalate, and the carbon monoxide and sulfur produced by the resulting reaction determined as previously described. The results of two runs are shown in the table.

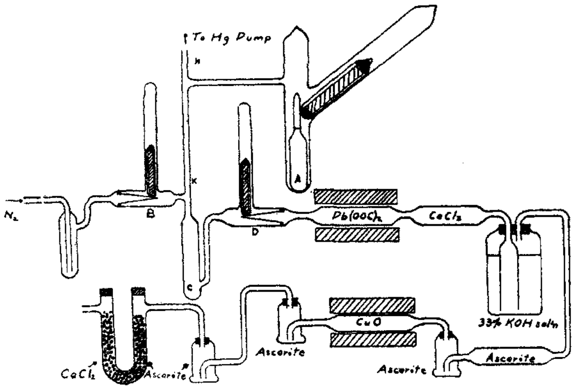

Fig. 1.

Experimental Data

	$SOCl_2$ taken	S_2Cl_2 taken	CO_2 from CO	$BaSO_4$ from S	$SOCl_2$ calcd.	Error, %
G.	2.4177	2.0329	1.3990	4.0369	2.412	0.2
Mole	0.02032		0.03180	0.01730	0.02027	
G.	2.7315	2.8066	1.5541	4.3370	2.729	0.1
Mole	0.02295		0.03532	0.01858	0.02293	

The fact that the over-all error is smaller than the error involved in the individual determination of either carbon monoxide (Section A) or sulfur (Section I) is largely due to the fact that the error in both of these latter determinations tended to be negative, so that when combined, partial cancellation took place.

Summary

1. From the heating curve of purified thionyl chloride a new value for the melting point of this compound, −101.4°, has been determined.

2. The reactions of thionyl chloride and of its thermal decomposition products, sulfur monochloride and dichloride, and chlorine, with lead oxalate have been quantitatively investigated at 60°, and the equations involved in the last three reactions have been determined.

3. The reactions of thionyl chloride and of sulfur monochloride with lead formate have been investigated quantitatively. Although no simple reaction was found to take place in these cases, mechanisms based on the known behavior of substances in analogous reactions have been suggested to account for the results.

4. Sulfur dioxide has been found to react with neither lead oxalate nor lead formate at 60°.

5. Based on the reactions with lead oxalate and the quantitative reduction of chlorine and sulfur dichloride to sulfur monochloride by means of elementary sulfur, a method has been developed for the determination of thionyl chloride in the presence of its thermal decomposition products with a precision of 0.2%.

Cambridge, Mass. Received October 24, 1934

[Contribution from the Chemical Laboratory of St. Louis University]

The Parachor and Structure of Nickel Carbonyl

By F. W. Laird and M. Alonza Smith, S.L.

The present determination of the surface tension of nickel carbonyl has been undertaken in order to compute its parachor and to secure thereby evidence as to its structure. Since previous determinations of its surface tension were made in the presence of its decomposition products,[1] we have been particularly careful to make our measurements upon specially purified material.

Thiophene-free benzene was repeatedly dried over calcium chloride and distilled from phosphorus pentoxide, the main fraction coming over at 79.9° (corr.). The water was redistilled from alkaline permanganate. The nickel carbonyl, prepared by one of us,[2] was redistilled in a vacuum in a cold room at −2°.[3]

The surface tension was measured by the two-capillary method of Sugden.[4] In preliminary standardizing measurements the surface tension of water was measured at 10, 15 and 20° and values of 74.26, 73.54 and 72.71 were obtained, as compared with the values of Young and Harkins[5] of 74.22, 73.49 and 72.75, respectively. Simi-

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[1] Ramsay and Shields, *J. Chem. Soc.*, **63**, 1089 (1893).

[2] F. W. Laird, *Rec. trav. chim.*, **46**, 177–180 (1927).

[3] Initial attempts at drying over phosphorus pentoxide gave spontaneous ignition.

[4] Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, 1930.

[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. IV, p. 447.

larly, with benzene, at 10, 15 and 20°, values of 30.22, 29.56 and 28.92 were obtained as compared with the values of Young and Harkins[5] (p. 454), of 30.22, 29.55 and 28.88, respectively.

The pure dry nickel carbonyl was distilled at $-2°$ into the apparatus which was connected with a mercury manometer. The apparatus was placed in a thermostat constant to $\pm 0.025°$ and the surface tension determined under its own vapor pressure at different temperatures. Two independent sets of measurements were made on successive samples of the material. The results are given in Table I.

TABLE I

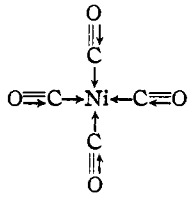
t, °C.....	8	14	20
γ.......	17.215	16.55	15.88
D^*......	1.34545	1.32446	1.31032
d^*......	0.00175	0.00238	0.00299
(P).....	258.75	260.40	260.65
Mean = 259.91.			

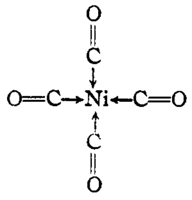
The densities D^* of the liquid were taken from the work of Mond and Nasini.[6] The vapor densities d^* were calculated from the vapor pressure measurements of Anderson,[7] assuming that the gas laws hold for nickel carbonyl vapor.

Discussion of Results

The value 259.9 for the parachor of nickel carbonyl is somewhat high compared to 250.8, the value calculated from the measurements of Ramsay and Shields.[1]

Experimental data[8] present strong evidence that (a) is the most probable structure for nickel carbonyl, though a resonance state between it and (b) is possible. Accepting (a) as the correct structure, the parachor of this should be four times that of CO plus that of Ni minus 4 × 1.6 for the four semi-polar links. Assuming that CO in the carbonyl has the same structure as free carbon monoxide, its parachor is 61.6 (the observed value for CO which presumably corresponds to resonance between $\mathrm{C{=}O}$ ($P = 48.0$) and $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$ ($P = 69.6$)), and that of the carbonyl is $240 + P_{\mathrm{Ni}}$. This gives (accepting 259.9 for $\mathrm{Ni(CO)_4}$) the value 19.9 for P_{Ni}, which is possible but not in agreement with Sugden's value.


(a)


(b)

Summary

The surface tension of nickel carbonyl has been measured at 8, 14 and 20° and found to be 17.21, 16.55 and 15.88 dynes, respectively. Assuming the generally accepted structure for nickel carbonyl, a value of 19.9 for P_{Ni} is obtained from the experimentally determined mean parachor, 259.9.

ST. LOUIS, MO. RECEIVED OCTOBER 24, 1934

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(6) Mond and Nasini, *Z. physik. Chem.*, **8**, 150 (1891).

(7) Anderson, *J. Chem. Soc.*, p. 1655 (1930).

(8) Sutton and Bentley, *Nature*, **130**, 314 (1932); Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1929, p. 216.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Thickness of a Surface Film of Copper

BY M. L. NICHOLS

In 1887 Oberbeck[1] reported the results of his experiments on the thickness of a film of metal which will give the same electromotive force as the massive metal. Using a very small current, the metal was plated electrolytically on a sheet of platinum and the electromotive force between this and another sheet of platinum was measured. On standing, the plated metal dissolved and as soon as any platinum was exposed, there was a rapid decrease in the electromotive force. By making a number of such experiments, he was able to determine the current and the time necessary to plate out the metal required for this point of rapid decrease of electromotive force. Then from Faraday's law, and on the assumptions that the metal was plated out evenly and free from hydrogen, and that it had the same density as the massive metal, he calculated the thickness of the layer of metal. He found the values of 2.32–2.73 mμ for zinc, 1.57–1.91 mμ for cadmium and 0.69–0.73 mμ for copper.

Bancroft states[2] that "since the metal was

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(1) Oberbeck, *Ann. Physik*, [3] **31**, 337 (1887).

(2) Bancroft, "Applied Colloid Chemistry," 1932, p. 455.