compound of intermediate composition. Whether any basic compound lies between $3SnCl_2.5SnO.3H_2O$ and the normal salt was not determined. The precipitates usually formed by the interaction of stannous chloride and water contain such a large proportion of stannic compound that the analyses are of no value in ascertaining the composition of the basic stannous chlorides.

In conclusion, I wish to express my indebtedness to Prof. Lash Miller, of the University of Toronto, who suggested this problem some years ago, and gave me considerable help with it.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE EFFECTS OF ACIDS AND BASES ON THE SURFACE ENERGY RELATIONS OF β,β-DICHLOROETHYLSULFIDE ("MUSTARD GAS").[1]

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This investigation was undertaken in order to determine the relative efficiencies of various substances in the emulsification of β,β-dichloroethylsulfide in water, and with the idea that the results obtained would be of importance in connection with a study of its physiological action. The importance of the effects of acids and bases on interfacial tension has been pointed out by Haber and Klemenciewicz.[2] An active part of a muscle is always electrically negative toward the part at rest, and the active muscle is acid in reaction while the resting muscle is slightly alkaline. An acid reaction always causes the phase which corresponds with the water at the water-benzene interface, to become negative, and in the muscle this aqueous phase is represented by the sarcoplasma in which the sarcostyles are imbedded. An interface of this nature acts as a hydrogen electrode, and it would seem probable that in addition to the change of electromotive force at the phase boundary, there should also be a change of surface tension near the neutral point with reference to the change from an acid to a basic reaction. The investigation which is commonly cited to show that laboratory experiments on simple two-phase systems seem to confirm this point of view, is that of von Lerch,[3] who, while working under Nernst's direction, found that the presence of sodium hydroxide at a concentration of 0.027 N in the aqueous phase, caused an extremely great lowering of the interfacial tension at the water-benzene phase boundary, a lowering amounting to 36%. At the request of Pro-

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[1] An investigation undertaken at the request of the National Research Council, and suggested to them by Lieutenant Colonel A. B. Lamb and Major R. E. Wilson.

[2] *Z. physik. Chem.*, 76, 385–431 (1909).

[3] *Drude's Ann.*, 9, 432 (1902).

fessor Haber the investigation was repeated by Harkins,[1] who found the results of von Lerch to be erroneous, and that at such concentrations bases do not lower the interfacial tension of the benzene-water system at all. The apparent lowering obtained by von Lerch was apparently due to the effects of the base upon the glass, which lowers the height of the liquid in a capillary tube when there is no lowering of surface tension caused by the base alone.

Benzene and saturated paraffin hydrocarbons are chemically too indifferent toward bases to give the surface tension lowering described in the last paragraph. Chloroform,[2] to some extent, and β,β-dichloroethylsulfide, much more markedly, give the lowering of interfacial tension toward water, when bases, but not when acids are added, and the magnitude of the actual effect is much greater than the fictitious one found by von Lerch. Thus 0.1 *N* sodium hydroxide solution reduces the interfacial tension at the water-dichloroethylsulfide phase-boundary by 55%.

The surface tension at 20° between β,β-dichloroethylsulfide and water is 28.36 dynes per cm., or about 5 dynes less than that between benzene and water. The surface tension of this liquid toward its vapor is 42.82 dynes per cm., which is 14 dynes higher than that of benzene. One of the most important characteristics of a liquid in this connection is the amount of work done when one square centimeter of the surface of the liquid approaches one square centimeter of a water surface. This value is 87.3 ergs in the case of β,β-dichloroethylsulfide, which indicates that this liquid, while only very slightly soluble in water, has a high attraction for it, although the magnitude of the work done is slightly less than that found for an alcohol. The following table (Table I) gives values for this work for a number of classes of organic substances:

TABLE I.

Liquid.	Work done ($-\Delta\gamma$) by the attractive forces between water and the liquid per sq. cm. of each.
Sulfur compounds	$-\Delta\gamma$
β,β-Dichloroethylsulfide	87.26
Mercaptan	68.50
Carbon disulfide	55.82
Octane	43.76
Benzene	66.63
Alcohols	93.0
Organic acids	95.0
Monochloroacetone	101.00
Dichloroacetone	90.28
Chloroform	67.30
Methylene chloride	71.00

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[1] Harkins, Davies, and Clark, THIS JOURNAL, 39, 548-9 (1917).

[2] N. D. Thatcher in this laboratory has obtained results which show that the surface tension at the interface water-chloropicrin is not lowered by either HCl or NaOH, but that a base lowers the tension at the chloroform-water interface.

According to the theory of Harkins,[1] the interfacial tension at a phase-boundary is lowered by any substance which makes the transition between the two phases more gradual with respect to the intermolecular electromagnetic fields.[2] A large number of substances might have been found which would have done this, but the only ones investigated were corn oil, Twitchell's solution, and turkey-red oil. All of these proved extremely effective in lowering the interfacial tension at the water-dichloroethylsulfide interface. The effectiveness of both the corn oil and the turkey-red oil were considerably increased by making the solutions alkaline with sodium carbonate at 0.1 N concentration, but this did not seem to be the case with Twitchell's solution. All of these substances proved to be remarkably effective as emulsifying agents, especially turkey-red oil, together with sodium carbonate.

Table II gives the results of the surface-tension determinations, which were made by the drop-weight method, using the proper precautions as determined by Harkins and Brown.[3] The radius of the tip used was 0.24995 cm. for all of the interfacial work, except when a 0.1% solution of turkey-red oil was used in the absence of sodium hydroxide, when the radius was 0.275 cm. For the dichloroethylsulfide alone a tip of 0.27441 cm. radius was used. The density of this latter liquid was 1.2732 g. per cc. In all of the experiments the aqueous solution was dropped upward through this liquid without allowing time for mixing.

TABLE II.

The Surface Tension between β,β-Dichloroethylsulfide and Various Aqueous Solutions in Dynes per Cm.

Substance.	Vol. of 1 drop in cc.	Density of substance.	r/a.	Surface tension.
Vapor	0.03555	.....	1.04	42.82
Water	0.1062	0.9982	0.595	28.36
0.1 N HCl	0.1090	1.00011	0.5385	28.90
0.1 N NaOH	0.04612	1.0032	0.8066	12.78
0.1 N Na_2CO_3	0.0695	1.0025	0.6635	18.82
1% Soln. turkey-red oil	0.0567	1.0000	0.607	14.47
1% Soln. turkey-red oil in 0.1 N Na_2CO_3	0.02977	1.0035	1.00	8.35
			$r/v^{1/3}$	
1% Twitchell's Soln.	0.04384	0.99924	0.7088	12.32
1% Twitchell's Soln. in 0.1 N Na_2CO_3	0.04663	1.00311	0.6944	12.89
1% Corn oil Soln.	0.4577	0.9984	0.698	12.94
1% Corn oil Soln. in 0.1 N Na_2CO_3	0.03936	1.0036	0.735	10.91

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[1] Harkins, Brown, Davies and Clark, THIS JOURNAL, **39**, 354–64, 541–96 (1917); Harkins and King, *Ibid.*, **41**, 970–92 (1919), especially pp. 480–3.

[2] The theory of Langmuir, which does not specifically refer to interfaces, leads to the same conclusions. See *Met. Chem. Eng.*, **15**, 468 (1916); *Proc. Nat. Acad. Sci.* **3**, 251–7 (1917); THIS JOURNAL, **39**, 1848–1906 (1917); see also Frankel, *Phil. Mag.*, **33**, 297 (1917) and especially Hardy, *Proc. Royal Soc.*, **86B**, 634 (1911–12).

[3] THIS JOURNAL, **41**, 499–524 (1919).

The values for r/a and $r/v^{1/3}$ indicate the shape of the drop. A discussion of this subject will be found in the paper of Harkins and Brown.

Table III gives data for the surface tension of a number of organic liquids prepared by Professor Huston of the Michigan State Agricultural College. Unfortunately, the two temperatures at which the measurements were made are not sufficiently far apart to give good values of the temperature coefficients. The tip used had a radius of 0.27441 cm.

TABLE III.

The Surface Tension of Some Organic Liquids.

Substance.	Temp.	Wt. of 1 drop in g.	Density.	$r/v^{1/3}$.	Surface tension. Dynes per cm.
Diphenyl propane	20°	0.03920	0.9998	0.808	37.15
$(C_6H_5)_2CHCH_2CH_3$	25°	0.03865	0.9962	0.801	36.64
1,1-Diphenyl ethane	20°	0.03975	1.0039	0.807	37.67
	25°	0.03925	0.9998	0.808	37.20
Diphenyl methane	26°	0.03963	1.0044	0.806	37.56
Ditolyl methane	20°	0.03745	0.9800	0.816	35.51
$(CH_3C_6H_4)_2CH_2$	25°	0.03670	0.9777	0.821	34.80
Propyl benzene or phenyl propane	20°	0.03396	1.0216	0.854	32.22
	25°	0.03299	1.0166	0.863	31.30

These liquids have a high surface tension for substances which contain carbon and hydrogen alone. It is apparent that the surface tension increases with the number of phenyl groups, with the degree of unsaturation, and with the decrease in the length of the paraffin chain. This is illustrated by the result of Jaeger, who obtains a much higher surface tension still for triphenyl methane, 44.7 dynes per cm. at 20°. Benzene has a much lower surface tension, which at 20° amounts to only 28.9 dynes per cm. The tolyl group increases the surface tension much less than the phenyl group. Former studies in this laboratory have also shown that the methyl group lessens the effect of phenyl groups, since the electromagnetic stray field around the methyl groups is much less, and this causes them to be oriented into the surface.

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