61.4

61.0

		TABLE III		
Appi	ACATION OF	F WALDEN'S	RULE TO SOL	IUM
	р-Осту	LBENZENESU	LFONATE	
Molality	Deg. C.	A (ohms ⁻¹)	$\frac{1}{10^{2}}$ $\frac{10^{2}}{13}$	$\Lambda \eta$
0.1	25	34.9	0.8949	31.2
	40	49.7	. 6536	32.5
	60	73.5	. 4699	34.5
0.005	25	68.7	0.8949	61.5

The method used is illustrated in Fig. 4 and the results are given in Table I which presents a comparison of CMC values obtained by the various methods. Because of the different temperatures involved, the comparisons are only approximate.

93.3

129.9

.6536

.4699

40

60



Fig. 4.-Specific conductance of sodium p-(1-methyldecyl)benzenesulfonate at 35°.

(13) "International Critical Tables," Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1927, p. 10.

Roughly, the surface tension method gives values which are 5-30% lower. On the other hand, the solubility method shows good agreement with the CMC's obtained from conductance, with the exception of one compound. The experimental data on this compound, 1-methyltetradecyl)-benzenesulfonate, have been carefully rechecked.

It has been stated previously⁴ that alkylarylsulfonates do not give slow draining films in the presence of organic additives. This conclusion was based on a study of commercial sulfonates. In the present study, we have found that slow draining films may be obtained in certain cases. The data in Table IV illustrate this point.

TABLE IV

FILM DRAINAGE TRANSITION TEMPERATURES FOR para-ALKYLBENZENESULFONATES WITH MYRISTYL ALCOHOL

$\stackrel{Molality}{ imes 10^2}$	Sulfonate, g./100 g. soln. Sodium p-(1-methyldecyl)- benzenesulfonate	Myristyl alcohol, g./100 g. soln. × 10 ²	Film drainage transition temp., °C.
0.224	0.0750	1 10	27.0
		0.75	26.4
		.40	24.0
111	0.0370	.55	41.5
		. 37	36.5
		. 18	4
	Sodium p-octylbense	nesulfonate	
1.37	0.4000	2.0	32.3
		1.0	30.0
		0.40	23.0
0.685	0.2000	1.0	43.1
		0.50	42.8
		. 20	33.6

^a Only fast draining film observed.

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REACTION HEATS OF ORGANIC HALOGEN COMPOUNDS. VIII. THE HEATS OF CHLORINATION OF PERFLUORINATED BUTENE-1. PENTENE-1 AND ISOBUTENE¹

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The heats of chlorination of perfluorobutene-1, perfluoroisobutene and perfluoropentene-1 have been measured in vapor phase reactions and found to be -44.97, -42.22 and -45.61 kcal./mole, respectively. Some physical properties of the reaction products together with their infrared absorption spectra have been determined. The thermochemical data are discussed in connection with the heats of chlorination of some simple perfluoroölefins.

In earlier papers^{2,3} we have described a calorimmeter which could be used to measure the heat of

(1) This research was supported by the Office of Scientific Research, Air Research and Development Command under Contract No. AF 18(600)-1151.

(2) J. R. Lachor, J. D. Park, et al., J. Am. Chem. Soc., 71, 1330 (1949).

(3) J. R. Lacher, J. D. Park, et al., ibid., 71, 1334 (1949).

vapor phase reactions. More recently⁴⁻⁶ we have modified it to permit the use of condensing vapor baths as a source of constant temperature. The present paper deals with the vapor phase heats of (4) J. R. Lacher, E. Emery, E. Bohmfalk and J. D. Park, THIS JOURNAL, 60, 492 (1956).

(5) J. R. Lacher, L. Casali and J. D. Park, ibid., 60, 608 (1956).

(6) J. R. Lacher, A. Kianpour and J. D. Park, ibid., 60, 1454 (1956).

Me

chlorination of perfluorinated butene-1, isobutene and pentene-1. The experimental procedures used were essentially those previously described.

Experimental Details .--- Perfluorobutene-1 and perfluoropentene-1 were prepared by the pyrolysis of the sodium salts of perfluorovaleric and perfluorohexanoic acids, respec-tively.⁷ The olefins were carefully purified by distillation in a Podbielniak column. The infrared spectra of the puri-fied material were identical to those reported in the litera-ture.⁸ Perfluoroisobutene was obtained as a gift from the Minnerte Minner Martin Martin the literature. Minnesota Mining and Manufacturing Company. It also was purified by repeated distillation in a 100-plate column. Infrared analysis of the various fractions suggested that the main impurity was perfluorobutene-2. We believe our product was 98 to 99% pure.

The catalyst consisted of ferric chloride on activated carbon. The carbon was sized to pass 6 and be retained on 14 mesh. After treatment with dilute hydrochloric acid, it was washed with water, dried at 120° and finally heated in vacuo at 350° for 24 hours. Twenty grams of ferric chloride was sublimed and then dissolved in 50 cc. of anhydrous ether. This solution was mixed with 120 g. of treated carbon. The ether was driven off by a stream of dry nitro-gen. The mixture was transferred to the calorimeter catalyst chamber and heated under vacuum at 120° for three hours. After cooling the catalyst chamber was filled with nitrogen and closed to the atmosphere.

In making a run, an excess of olefin was used. The re-action was quantitative and no chlorine could be detected in the exit line by means of the potassium iodide-starch paper test. The rate of formation of product was taken to be equal to the rate of consumption of chlorine. This was determined by diverting the chlorine to a collecting tower filled with glass beads for a known length of time. The gas was absorbed in a 3 N potassium iodide solution and the iodine which was liberated was titrated with standard sodium thiosulfate in the usual way.

The products of the reactions were distilled in a micro-Podbielniak column and some physical properties measured which are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF PERHALOALKANES

Compound	B.p., °C. (760 mm.)	Density at 20°	Refractive Index at 10°
CF ₃ CF ₂ CF ₂ CFClCF ₂ Cl	85	1.7225	1.3095
CF ₃ CF ₂ CFClCF ₂ Cl	67	1.6695	1.3082
CF ₂ CCICF ₂ Cl	65	1.708	1.3118
CF ₃			

Their infrared absorption spectra are shown in Fig. 1. Perfluorobutene-1 and pentene-I were chlorinated photo-chemically in the vapor phase. The infrared spectra of the products were identical to those produced by catalytic chlorination.

The results obtained on calorimetric runs which were carried out without experimental difficulty are given in Table II. It would have been desirable to have made more runs on each of the compounds; however, sufficient material was not available.

Discussion of Results .- The data obtained in these experiments together with the chlorinations previously reported^{2,3} are summarized in Table III. For this series of compounds there are strong

deviations from the additivity rule. The heat of chlorination of tetrafluoroethylene is strongly exothermic being 57,323 cal./mole as compared to 43,600 cal./mole⁹ shown by ethylene. When one fluorine is replaced by a trifluoromethyl group, the heat of reaction drops 10 kcal. Within experi-

(7) J. D. Lazerte, L. J. Hals, T. S. Reid and G. H. Smith, J. Am.

Chem. Soc., 75, 4525 (1953). (8) "Fluorine Chemistry," Vol. II, J. H. Simons, editor, Academic Press, Inc., New York, N. Y., 1954.

(9) J. D. Conn, G. B. Kistiakowsky and E. Smith, J. Am. Chem. Soc., 60, 2764 (1938).





TABLE II

CHLORINATION OF PERFLUOROÖLEFINS AT 128°

les/min. $\times 10^4$	cal./min.	cal./mole
(a)	Perfluoropenten	e-1
1.195	5.478	45,841
1.298	5.876	45,503
2.041	9.389	46,002
1.955	8.819	45,109
Δ.	$H_{\rm av} = 45.61 \pm 0.01$	40 kcal./mole
(b) Perfluorobutene	-1
1.465	6.527	44,698
1.694	7.618	44,970
1.408	6.369	45,234
-Δ.	$H_{\rm av} = 44.97 \pm 0.$	31 kcal./mole
(c)) Perfluoroisobute	ene
2.298	9.770	42,552
1.899	7.920	41,706
2.070	8.782	42,415
1.390	5.867	42,217
	$\Delta H_{av} = 42.22 \pm$	0.51 kcal./mole

TABLE III

VAPOR PHASE HEATS OF CHLORINATION AT 128° $-\Delta H$, cal./mole Compound

Compound	
$CF_2 \longrightarrow CF_2$	57,323
CF2=CF-CF3	47,149
CF ₂ =CF-CF ₂ -CF ₃	44,966
CF ₂ =CF-CF ₂ -CF ₂ -CF ₃	45,612
$CF_2 = C < CF_3$	42,222
CF=CF	
CF-CF-	37,376
CF ₂ =CFCl	48,815
CF.=CCl.	41.076

mental error, a perfluoroethyl and perfluoropropyl group give the same drop of about 12 kcal. When both trifluoromethyl groups are on the same carbon, the lowering of the heat of chlorination is 15 kcal.; with a cyclobutene the lowering is 20 kcal. A chlorine atom is less effective if only one

is present. One gives a lowering of 8.5 kcal, but two on the same carbon gives a lowering of 16.2 kcal.

THE ELECTROCHEMICAL DOUBLE LAYER ON SILVER SULFIDE¹

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Adsorption densities of silver and sulfide ions at the silver sulfide-solution interface were determined as a function of pAg and ionic strength. Silver and sulfide ions were identified as the potential determining ions for this system. The zero-point-of-charge for silver sulfide in solutions containing sodium acetate and sodium metaborate was observed to lie at pAg 10. This zero-point-of-charge was also shown to be independent of the concentration of hydrosulfide ions below 10^{-9} mole/liter and of pH in the pH range 4.7 to 9.2. From the adsorption data the magnitude of the changes in free energy at the solid-liquid interface was calculated at different pAg values. The differential capacity of the double layer was determined from the adsorption curves. The results indicated that the capacity values were in good agreement with those found for silver iodide and mercury except at high positive polarization of the surface.

Introduction

In the separation of a valuable mineral from the worthless solids by means of the froth flotation process, reactions at the solid-solution and solid-air interfaces are very important.² The reagents used in flotation vary widely in their chemical nature and in the effects they produce at the solid interfaces. The mechanisms by which these changes are accomplished are not clearly understood and have been the subject of much investigation in recent years.

One approach to this problem would be to attempt a correlation between the electrical properties of a specific solid-liquid interface under a given set of conditions and the flotation behavior of the same solid under identical conditions. The desirability of such a correlation has been recognized for a long while and a few experiments have been carried out.³⁻⁶ However, the success of this approach until now has been limited by the lack of quantitative knowledge of the electrical properties of the solid-liquid system except for the mercurysolution' and silver iodide-solution system.⁸ Neither one of these two systems is of much practical interest from a flotation standpoint.

A program of research was initiated to study the electrical and electrochemical properties of a solid– liquid system which is more closely allied to flotation practice. The solid chosen was silver sulfide and this paper reports the results of an electrochemical study of the adsorption of silver and sulfur-bearing ions at the silver sulfide-solution interface in the presence of controlled concentrations of an indifferent electrolyte.

Silver sulfide was chosen as the solid because it is a heavy metal sulfide typical of the ore-forming

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(3) D. Talmud and N. M. Lubman, Kolloid-Z., 80, 163 (1930).

(4) P. A. Lintern and N. K. Adam, Trans. Faraday Soc., 31, 564 (1935).

(6) O. Jo, J. Mining Inst. Japan, 68, 439 (1952).

(8) E. L. Mackor, Rec. trav. chim., 70, 763 (1951),

metal sulfides; because in contact with silver it forms a reversible electrode of the second kind; because it can be prepared as a well flocculated precipitate with high specific surface and because silver has only one important valence state, which simplifies greatly the interpretation of electrochemical results.

Experimental

The experimental technique adopted in this research is similar to that used by Mackor⁸ for his studies on silver iodide. This technique consists of adding measured quantities of silver acetate to an aqueous suspension of finely divided silver sulfide and then determining electrochemically the concentration of silver ion in solution after equilibrium has been reached. The amount adsorbed at the solid surface is determined by difference.

Materials.—Finely divided silver sulfide was prepared by precipitation with hydrogen sulfide from an ammoniacal solution of silver hydroxide.⁹ After precipitation, the silver sulfide was allowed to stand overnight in contact with the saturated hydrosulfide solution. The precipitate was then washed free of foreign electrolytes by decantation. The precipitation and subsequent washings were carried out as much as possible in a nitrogen atmosphere. Chemical analyses of two of the precipitates gave 86.99 and .86.12% silver and 13.48 and 12.96% sulfur, respectively. Stoichiometrically, silver sulfide should analyze 87.1% silver and 12.9% sulfur. X-Ray diffraction patterns of these two precipitates checked with the data listed by the A.S.T.M. for *f*-silver sulfide, the low temperature form of silver sulfide. A value of 7.32 g./cm.³ was used for the density of silver sulfide. The aging characteristics of several precipitates were checked by measuring electrochemically the change in silver ion concentration in a solution in contact with the precipitate for periods up to six days. This check was necessary because the experimental technique required that the solid should not change its specific surface by recrystallization at a rapid rate. The aging tests showed that during the time of testing, the precipitates decreased in surface area by only a few hundredths of one per cent. A precipitate was used in an experiment for about fourteen days and was not re-used.

Tank prepurified nitrogen which was further purified, provided an inert atmosphere for the electrochemical titrations and was used to remove dissolved oxygen from the solutions. The tank nitrogen was purified by passing it over hot copper punchings, then through a solution of chromous chloride, next over activated charcoal and finally through a suspension of silver sulfide of the same composition as the one being titrated at that time.

Tank hydrogen sulfide, purified according to the recommendation of Dodd and Robinson,¹⁰ was used as a source of

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Chemistry," Elsevier Publishing Co., New York, N. Y., 1954.

⁽⁵⁾ B. Kamienski, Z. physik. Chem., A158, 441 (1932).

⁽⁷⁾ D. C. Grahame, Chem. Revs., 41, 441 (1947).