be readily used as a source for synthetic work in the phenanthrene and related series.[3]

Acknowledgment.—Thanks are due to the Southern Pine Chemical Company, Jacksonville, Florida, for a supply of retene used in this investigation.

Experimental

1-Methylphenanthrene.[4]—Two hundred and fifty grams of retene and 50 g. of dehydrated fuller's earth were refluxed for nine hours. The gas developed was passed over bromine and in time was transformed into a colorless liquid. After cooling the semisolid brownish reaction product containing fuller's earth was dissolved in hexane and filtered. The filtrate was evaporated to remove most of the solvent and residues left standing in the ice box overnight after which the separated brownish colored crude hydrocarbon was removed by filtration; yield of crude material 97 g. This was recrystallized from hexane as fine glistening scales, m. p. 122–122.5° (cor.).

Anal.[5] Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.55; H, 6.36.

The hexane solution from the above operation was evaporated and 118 g. of the residue was fractionated once in vacuum at 1 mm. pressure: I, 155–165°, 78 g. (solidified on standing); II, 165–175°, 20 g. (non-solidifying oil); III, 18 g. of residue. Only the first fraction was investigated at this time. It was recrystallized from hexane, m. p. 122–123° (cor.), and was found to be 1-methylphenanthrene since it did not depress the melting point of the analytical sample.

The 250 g. of retene yielded 62 g. of pure 1-methylphenanthrene.

The bromine absorption product was washed first with an aqueous sodium sulfite solution, then with a sodium carbonate solution and with water. The colorless liquid of propylene bromide was dried with anhydrous sodium sulfate and fractionated at ordinary pressure: b. p. 142–143° (uncor.); d_{20} 1.9297; n^{20}_{D} 1.52604.

Anal. Calcd. for: $C_3H_6Br_2$: Br, 79.16; Found: Br, 79.54.

Picrate of 1-Methylphenanthrene.—Brick red needles, recrystallized from alcohol, m. p. 139° (cor.).

Anal. Calcd. for: $C_{21}H_{15}O_7N_3$: N, 9.97. Found: N, 9.89.

The hydrocarbon recovered from the picrate melted at 122–122.5°.

1-Methylphenanthroquinone.—Dark reddish-brown needles, recrystallized from acetic acid, m. p. 192–193° decompn. (cor.).

Anal. Calcd. for: $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.10; H, 4.54.

In cold concentrated sulfuric acid it dissolved to a dark green solution, which color disappeared upon dilution.

Phenazine.—Fluffy slightly yellowish needles recrystallized from glacial acetic acid, m. p. 183.5° (cor.).

Anal. Calcd. for: $C_{21}H_{14}N_2$: N, 9.52. Found: N, 9.97.

In cold concentrated sulfuric acid solution the color was burgundy red, which was lost on dilution.

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[3] Preliminary tests have shown, as expected, that 1-methylphenanthrene may be readily subjected to the Friedel–Crafts reactions, sulfonation, halogenation, etc.

[4] Subject matter for a U. S. Patent application.

[5] All analyses by Mr. S. Gottlieb, Columbia University, N. Y.

The Solubility of Carbon Dioxide in Aqueous Solutions of Sulfuric and Perchloric Acids at 25°

BY AARON E. MARKHAM AND KENNETH A. KOBE

The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions was recently reported by Markham and Kobe.[1] They found that the gas solubility isotherms could be fitted by an equation of the form

$$\frac{S}{S_0} = am + \frac{1}{1 + bm} \qquad (1)$$

in which S is the unit solubility, cc. gas (sc) dissolved by the amount of solution containing one gram of water, m is the salt molality, a and b are empirical constants derived from the data and specific for each curve. This equation fitted the isotherms within the limits of experimental error, about 0.2%, over the entire range of salt concentrations, up to 8 molal for sodium nitrate solutions.

It was the purpose of this work to determine the solubility of carbon dioxide in an aqueous solution of a strong electrolyte that is miscible in all proportions with water and whose gas solubility isotherm is not a continually decreasing function, as is the case with solutions of salts, and determine the range over which equation 1 can be fitted to the data.

Method and Results

Perchloric and sulfuric acids were Baker C. P. analyzed (A. C. S. specifications). The concentrated acid was standardized and diluted to give the desired solution, which was checked by a density determination.[2] The 100% sulfuric acid was made by adding fuming acid to the concentrated acid. The apparatus and technique were those described in the previous paper.[1] All measurements were made at a temperature of 25° and a partial gas pressure of 760 mm. The results are given in Table I. The Bunsen coefficient, α,

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[1] Markham and Kobe, THIS JOURNAL, **63**, 449 (1941).

[2] For aqueous solutions of perchloric acid at 25°, see Markham, *ibid.*, **63**, 874 (1941).

TABLE I

SOLUBILITY OF CARBON DIOXIDE IN ACID SOLUTIONS AT 25°

H_2SO_4, *m*	Mole %	α	*S*	$S_{calcd.}$
0.0	0	0.7565	0.7587	
0.5	0.8928	.6983	.7127	0.7183
1.0	1.7697	.6650	.6911	.6911
2.0	3.4779	.6132	.6610	.6642
3.0	5.1277	.5854	.6546	.6619
4.0	6.7220	.5740	.6659	.6757
6.0	9.7551	.5878	.7332	.7332
8.0	12.597	.6159	.8238	.8154
10.0	15.266	.6337	.9053	.9116
14.15	20.32	.6404	1.0372	1.1372
18.86	25.37	.6225	1.1453	
28.29	33.77	.5840	1.3386	
37.72	40.48	.5659	1.5573	
56.58	50.49	.5741	2.1232	
94.30	62.95	.645		
188.6	77.26	.753		
282.9	83.60	.813		
565.8	91.07	.880		
1131.6	95.32	.920		
	100	.960		
$HClO_4$				
0.0	0.0000	0.7565	0.7587	
.25	.4484	.753	.764	0.771
.50	.8928	.759	.778	.783
.75	1.3332	.765	.793	.796
1.00	1.7697	.772	.809	.809
1.50	2.6313	.785	.840	.835
2.00	3.4779	.798	.865	.861
4.00	6.7220	.835	.984	.973
6.00	9.7551	.863	1.091	1.091
10.00	15.266	.866	1.239	1.343
15.47	21.79	.762	1.264	
22.84	29.15	.718	1.426	

Constants for Equation 1

	a	*b*
H_2SO_4	0.0885	0.2159
$HClO_4$	.107	.04284

has been plotted against the weight and mole per cent. of acid in Fig. 1.

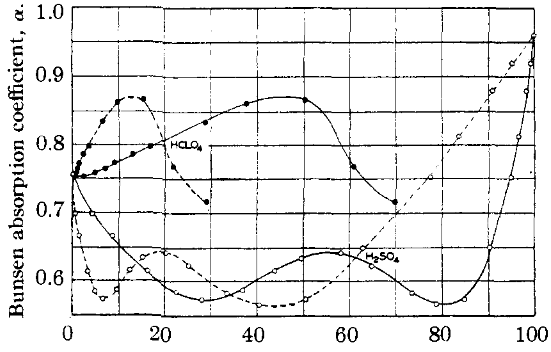

Fig. 1.—Bunsen coefficient for carbon dioxide in solutions of sulfuric and perchloric acids at 25°: ——, weight per cent.; – – – –, mole per cent.

The solubility of carbon dioxide in concentrations of perchloric acid up to six molal, and in sulfuric acid up to ten molal, fits equation 1 with a maximum error of about 1%. The values calculated are given in Table I as $S_{calcd.}$. From the curves it is seen that the equation no longer fits the data after the solubility passes through the first maximum point, though the first minimum point in the sulfuric acid solution is fitted well by the calculated values. The maxima and minima in the gas solubility curves do not correspond to simple compounds of the acid with water.

Equation 1 represents a hyperbola which goes to positive infinity at $-1/b$ and becomes tangent to the line S_0am at the other extremity; the equation can account only for a minimum, as with sulfuric acid, but not for a maximum, in any actual isotherm.

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Recovery of the Cottonseed Allergenic Protein from its Picrate by Electrophoresis

BY JOSEPH R. SPIES

In a recent communication a chemical method for recovering the cottonseed allergenic protein CS-13A from its picrate was described.[1]

Incidental to a large scale electrophoretic separation of the allergenic fraction CS-1A it was found that the protein CS-13A could be recovered from its picrate by high voltage electrophoresis.[2,3,4] Advantage was taken of the fact that the protein picrate was soluble in 50% dioxane, in which the freed protein was insoluble. In this solution picric acid migrated toward the anode cell and the protein moved to the cathode cell where it precipitated.

Experimental

The electrophoresis apparatus used for the separation consisted of a series of six cells made from 125 ml. Erlenmeyer flasks with 10 mm. side tubes sealed on 25 mm. above the bottom. Cells were joined by 25 mm. lengths of heavy walled gum rubber tubing. Temperature was

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[1] Spies, Coulson, Bernton and Stevens, THIS JOURNAL, **62**, 1420 (1940).

[2] The theory and an application of high-voltage electrophoresis have been described by R. J. Williams and J. H. Truesdail, *ibid.*, **53**, 4171 (1931). See also later papers by Williams and co-workers.

[3] V. du Vigneaud, G. W. Irving, H. Dyer and R. R. Sealock, *J. Biol. Chem.*, **123**, 45 (1938), have used high voltage electrophoresis in fractionating the posterior pituitary hormone.

[4] E. Gebauer-Fuelnegg and A. I. Kendall, *Ber.*, **64**, 1070 (1931), separated the strongly basic histamine from the dipicrate by electrodialysis using direct current at 110 v.