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O.M. REEL

B.M. 30

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Report by Dr. Feiler

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THE SOLUBILITY OF CARBON DIOXIDE, SULFUR DIOXIDE AND HYDROGEN SULFIDE IN ORGANIC LIQUIDS.

NITROGEN DIVISION/HYDROCARBON RESEARCH, OPPAU
September 1, 1938

Translation by D. M. Mason
April 11, 1946

eh/

THE SOLUBILITY OF CARBON DIOXIDE, SULFUR DIOXIDE AND HYDROGEN SULFIDE IN ORGANIC LIQUIDS.

Contents

I. INTRODUCTION

Carbon dioxide, sulfur dioxide, and hydrogen sulfide, alone or as constituents of technical gas mixtures, frequently come in contact with organic liquids. Thus, it is important to know the solubility relationships concerned. Moreover, it was of interest to study these relationships from the standpoint of the possibility of separating these gases from one another or from other gas mixtures by simple washing with organic liquids. Systematic investigation in this direction appears to be important, since much experience has generally shown that carbon dioxide, sulfur dioxide and hydrogen sulfide show quite considerable solubility not only in water, but also in organic liquids.

In this connection, it may be noted that washing processes for CO_2, SO_2, and H_2S whereby easily decomposed compounds are formed, are already known. Of special concern here, are the "Alkazid" process of the I.G. Farbenindustrie, according to which CO_2 and H_2S are absorbed by solutions of strong inorganic bases with weak organic acids (1) and processes in which SO_2 is absorbed by organic bases (2). Examples of the latter are the "Sulfidin" process of the Metallgesellschaft A.G., and the phenolate process of the Koppers Co., Pittsburgh, in which CO_2 and H_2S are separated from gas mixtures by means of mixtures of strong organic bases with phenols.

Processes such as the above, which depend upon chemical binding of the gas, are not considered in the present work. Here the purely physical solubility of CO_2, SO_2, and H_2S in a great number of organic liquids has been systematically investigated, relationships clarified and practical applications verified, especially in relation to the purification and separation of technical gas mixtures.

(1) Chemische Fabrik 1938, p. 283.
(2) Metallgesellschaft A.G.: DRP606447, 621529, 621760, 623018, 645879.
Ges f. chem. Industrie: DRP557723.
J.C.J.: E.P.371868.
Ciba: F.P.695200, E.P.339926.
Boswell and Buel: AP2047819.

II. GASES USED

The following gases were used:

CO_2, cylinder	99%
SO_2, cylinder, washed with concentrated sulfuric acid	100%
H_2S, from iron sulfide, washed with water, liquefied, distilled and led over calcium chloride	99%

III. SOLVENTS USED

Organic liquids were collected as extensively as possible for the absorption experiments, except in cases of too high a vapor tension, too high a viscosity or too high a price.

IV. APPARATUS, EXPERIMENTAL METHODS AND EXPRESSION OF RESULTS

The absorptions were all carried out at 20°C. and atmospheric pressure and expressed as already described in "The Solubility of Gaseous Hydrocarbons in Organic Liquids" by Dr. Feiler (Nitrogen Division report of July 1, 1937).

In this report also, the solubility is expressed as gas volume in cc., reduced to standard conditions, absorbed by 1 cc. of liquid. The values are shown below in tables(1). Table A: Aliphatic Organic Liquids; Table B: Aromatic Organic Liquids; Table C: Heterocyclic Organic Liquids. In Tables D, E and F, are shown the 25 best solvents for each of the three gases, together with the corresponding solubility values.

V. EXPERIMENTAL RESULTS

The absorption experiments (see tables) carried out with CO_2, SO_2, and H_2S in organic liquids at 20°C. under atmospheric pressure show the following:

1. The solubility of CO_2, SO_2, and H_2S is considerably higher in most organic liquids than in water and in most cases is several times that of water; thus in several cases there is absorbed at 20°C. and one atmosphere pressure by 1 cc.:

   CO_2: Over 5 cc. (Water 0.88 cc.).
   SO_2: Over 200 cc. (Water 39.37 cc.).
   H_2S: Over 29 cc. (Water 2.58 cc.).

2. These gases react with different organic liquids as already known in part; thus the following reactions occur:

   CO_2 with aliphatic amines, benzyl amine, and piperidine;
   SO_2 with amines, pyridine, piperidine, "quinaldine", aldehydes, and alkyl alcohols;
   H_2S with amines, piperidine, several aldehydes and ketones such as benzaldehyde, o-chlorobenzaldehyde, cyclohexanone, aldol, acrolein, pyruvic acid, furfural, as well as with diethyl sulfate.

(1) Footnote 1 (in the tables) indicates an increase due to high vapor tension, and footnote 2 indicates reaction of the gas with the solvent.

The reaction with organic bases is the basis for the "sulfidin" and "alkazid" processes (see introduction).

3. The comparative solubilities of CO_2, SO_2, and H_2S in organic liquids range as follows:

Solubility of H_2S is 5-10X solubility of CO_2.

Solubility of SO_2 is (5-15X solubility of H_2S. (20-100X solubility of CO_2.

4. The solubilities of CO_2, SO_2, and H_2S in organic liquids are comparable to gaseous hydrocarbons as follows:

Solubility of CO_2 approximates the solubility of ethylene and ethane.
Solubility of H_2S approximates the solubility of propylene and propane.
Solubility of SO_2 approximates the solubility of butylene and butane.

The removal of CO_2, H_2S, and SO_2 from gaseous hydrocarbon mixtures is, therefore, only difficultly possible.

5. Organic liquids which contain the carbonyl or carboxyl group and especially esters and acids (provided they do not react) are especially suited as purely physical solvents for these gases. For the individual gases the following are especially suited:

CO_2: Aldehydes, ketones, acids, esters and their derivatives, as well as pyridine and acetonitrile, formamide and quinoline.

H_2S: Several ketones, esters and their derivatives, as well as pyridine, acetonitrile, quinaldine, and quinoline.

For each of the three gases, the 25 best solvents with the solubility values are given in respective tables D, E, and F.

VI. SUMMARY

The solubility of CO_2, SO_2, and H_2S in a great many organic liquids at atmospheric pressure and 20° has been obtained. It has been shown that in most cases the solubility of these gases is many times that in water, so that enrichment or removal of these gases from gas mixtures by physical absorption in organic liquids and subsequent desorption appears possible. Organic liquids containing carbonyl or carboxyl groups, especially esters, are best suited as such purely physical solvents. Reactions between these gases and solvents, such as between CO_2 and aliphatic amines or SO_2 and aromatic amines, have not been further investigated here.

In especially favorable cases of purely physical solvents, it is planned to carry out experiments directed toward the practical separation of the gases from technical gas mixtures.

This work was carried out in 1937.

Translation by:
D. M. Mason
4/11/46: eh/

TABLE A

Aliphatic Compounds	Quantity of gas in cc. (reduced to standard conditions) absorbed at 20°C. and 1 atmosphere by 1 cc. of liquid.		
	CO_2	SO_2	H_2S
Hydrocarbons			
Hexane	(1)	5.64	3.63
Heptane	0.94	9.25	5.95
Isooctane (2.2.4 trimethyl pentane)	0.93	8.6	5.1
Iso-octene (trimethyl pentene-1)	1.14	25.4	7.02
Petroleum ether	(1)	(1)	(1)
Benzine	(1)	6.79	4.0
Normal benzine	(1)	6.36	4.34
Ligroin (BP 100-150°)	1.15	14.39	6.5
Petroleum	1.16	12.33	5.84
Halogen Compounds			
Methylene chloride	(1)	44.3	5.6
Chloroform	(1)	41.5	12.1
Bromoform	1.27	27.55	17.5
Carbon tetrachloride	0.35	15.21	7.23
Ethylene chloride	2.07	93.55	16.92
Ethylene dichloride	(1)	28.9	5.76
Ethylene trichloride	1.46	53.2	10.5
Ethylene tetrachloride	1.69	17.0	8.0
Trichlorethane	2.78	69.9	16.15
Tetrachlorethane	2.36	53.0	15.23
Pentachlorethane	2.10	26.6	11.12
Ethylene bromide	1.78	64.1	17.2
Propylene bromide	1.96	52.8	14.66
Ethyl iodide	(1)	49.6	14.02
Butyl iodide	1.78	39.4	13.97
Allyl chloride	(1)	48.0	6.22
Amine Compounds and Their Derivatives			
Formamide	1.78	241.9	7.33
Methyl amine	(2)	(2)	(2)
Triethyl amine	(2)	(2)	14.67
Ethylene diamine	(2)	(2)	(2)
Alcohols and Their Halogen Derivatives			
Methanol	2.07	19.77	14.14
Ethanol	1.79	113.1	10.44
n-propyl alcohol	2.01	82.6	10.8
Isopropyl alcohol	1.47	77.0	9.15
n-butyl alcohol	1.96	68.0	9.73
Isobutyl alcohol	1.77	93.7	8.33
Isoamyl alcohol	1.93	86.2	8.33
n-hexyl alcohol	1.75	52.9	8.64
Octyl alcohol	1.31	32.4	7.32
Allyl alcohol	2.37	(2)	11.63
Ethylene glycol	1.15	109.6	6.52
Butylene glycol	1.19	84.7	6.87

TABLE A (con.)

	CO_2	SO_2	H_2S
Ethylene chlorhydrin	3.35	126.0	12.39
Epichlorhydrin	3.72	226.6	19.45
Dichlorhydrin	2.00	85.4	11.43
Ethers			
Ethyl ether	(1)	31.8	6.17
Isoamyl ether	1.83	89.4	9.06
B, B'dichloroethyl ether	2.47	118.9	16.65
Aldehydes and Their Derivatives			
Formaldehyd (30% Solution)	1.83	(1)	(1)
Paraldehyde	2.79	(2)	13.7
Ketones and Their Derivatives			
Acetone	1.96	231.7	20.35
Acetylacetone	4.17	185.6	17.84
Methyl ethyl ketone	3.48	224.2	25.3
Diisopropyl ketone	3.26	122.1	17.16
Aldol	0.69	(1)	(2)
Acrolein	0.45	231.5	(2)
Chloroacetone	3.49	192.5	17.5
Acids, Saturated Monobasic			
Formic acid	2.25	98.7	5.31
Acetic acid	4.15	144.6	12.21
Acetic anhydride	5.12	217.6	16.06
Propionic acid	3.95	99.3	12.03
Butyric acid	3.39	70.8	11.33
Valeric acid	3.03	56.6	10.13
Pyruvic acid (?) (Brenztraubensaure)	0.53	72.7	—
Acids, Unsaturated Monobasic			
Acrylic acid	1.45	66.1	6.04
Oleic acid	1.14	20.0	6.14
Halogen Substituted Fatty Acids			
Dichloroacetic acid	2.51	67.6	10.13
Chloroacetyl chloride	(1)	89.7	8.1
Acid Chlorides and Acid Amides			
Acetyl chloride	(1)	87.3	7.6
Esters			
Methyl formate	—	153.1	9.97
Ethyl formate	1.29	153.1	13.0
Propyl formate	2.09	163.0	16.65
Methyl acetate	2.40	231.0	17.25
Ethyl acetate	4.17	107.7	20.55
Propyl acetate	4.25	166.3	20.2
n-butyl acetate	6.19	143.3	18.6
Isoamyl acetate	4.02	125.9	17.25
Methyl propionate	3.91	186.6	19.7

TABLE A (con.)

	CO_2	SO_2	H_2S
Ethyl propionate	2.27	169.2	20.5
Ethyl butyrate	4.02	158.3	18.3
Diethyl oxalate	4.31	176.6	17.2
Ethyl malonate	4.11	170.4	17.65
Glycol monoacetate	3.36	206.8	15.47
Glycol diacetate	4.49	224.0	17.7
Methyl glycol acetate	5.12	265.8	24.2
Ethyl glycol acetate	4.63	209.8	23.1
Butyl glycol acetate	3.77	159.8	19.05
Diethyl malonate	4.0	170.0	17.3
Ethyl succinate	3.84	165.3	16.3
Acetoacetic ester	4.14	197.4	17.95
Acetonitrile	5.59	280.0	20.28
Ethyl chloroacetate	3.73	144.1	17.1
Ethyl chloroformate	3.56	103.9	12.75
Dimethyl sulfate	4.09	178.1	12.63
Diethyl sulfate	3.48	137.4	—
Sulfur Compounds			
Carbon disulfide	(1)	0.86	1.61
Fats, Oils, and Waxes			
Pine oil	1.42	27.1	8.02
Linseed oil	1.45	35.6	8.27
Olive Oil	1.27	30.0	7.47
Sesame oil	1.23	(2)	(2)
Turpentine oil	1.46	28.1	7.32
Neats foot oil	1.26	31.5	7.01
Rapeseed oil	1.21	29.2	7.13

TABLE B

AROMATIC COMPOUNDS

Hydrocarbons	CGR	SOR	HeS
Benzene	0.61	79.9	1.51
Toluene	1.33	83.3	13.73
Ethyl benzene	1.35	89.4	12.63
Cumene	1.51	85.6	10.73
Styrene	1.32	74.6	13.3
Xylene (Mixed)	1.33	79.3	12.4
Mesitylene	1.76	82.6	10.72
Pseudo cumene	1.74	76.8	11.35
p cymene	1.59	80.0	10.39
Cyclohexene	(1)	8.0	5.23
Tetralin	1.2	85.5	10.6
α-methyl naphthalene	1.12	66.2	10.72
Halogen Derivatives of Hydrocarbons			
Chlorobenzene	2.0	89.1	12.74
Bromobenzene	1.73	82.2	12.76
Iodobenzene	1.19	40.2	12.0
Benzyl chloride	1.73	75.1	12.7
Benzal chloride	1.65	80.0	11.38
Toluene trichloride	1.85	29.5	8.76
o-Dichloro benzene	1.65	39.9	10.0
o-Chlorotoluene	1.79	61.0	10.92
m-Chlorotoluene	1.75	61.0	10.66
p-Chlorotoluene	1.87	62.4	11.1
o-bromotoluene	1.63	69.2	11.4
Trichlorobenzene	1.67	25.2	8.18
α-Chloronaphthalene	0.96	40.0	8.64
α-Bromnaphthalene	0.93	35.0	8.47
Nitro Derivatives of Hydrocarbons			
Nitro benzene	2.44	108.4	12.4
o-nitrotoluene	2.25	95.4	11.62
m-nitrotoluene	2.15	92.5	11.2
Aromatic Ethers			
Anicole	2.36	150.0	15.2
Phenetole	1.52	92.9	13.15
Anisidine	1.24	(2)	13.03
Amino and Azo Compounds			
Aniline	1.36	(2)	13.10
Methyl aniline	1.22	(2)	14.73
Dimethylaniline	1.39	(2)	15.03
Monoethylaniline	1.24	(2)	13.06
Diethylaniline	1.33	(2)	12.6
o-Toluidine	1.4	(2)	13.4
m-Toluidine	1.46	(2)	13.34
Xylidine	1.52	(2)	13.1
o-chloroaniline	1.31	157.3	14.4

TABLE B (con.)

	CO_2	SO_2	N_2
m-chloroaniline	1.42	(2)	13.95
Benzylamine	(2)	(2)	(2)
Cresols and Their Derivatives			
m-Cresol	1.35	92.6	10.48
o-chlorophenol	1.73	68.3	13.0
Aromatic Alcohols			
Cyclohexanol	1.22	52.8	8.46
Methyl cyclohexanol	1.03	42.3	7.48
Benzyl alcohol	1.35	94.7	10.52
Aldehydes			
Benzaldehyde	2.74	197.1	(2)
o-chlorobenzaldehyde	2.21	105.4	(2)
Ketones			
Cyclohexanone	3.04	211.2	(2)
Acids and Their Derivatives			
Benzoyl chloride	2.09	62.2	10.47
Esters			
Ethyl benzoate	2.88	107.8	14.3
Ethyl cinnamate	2.09	95.9	13.3
Methyl salicylate	2.53	90.1	11.2
Trioresyl phosphate	1.22	73.4	10.6
Ethyl salicylate	2.33	78.3	10.94
Terpenes			
Dipentene	1.49	42.4	9.0
Limonene	1.52	83.6	10.15

TABLE C

HETEROCYCLIC COMPOUNDS

Heterocyclic Compounds			
Furfural	3.43	172.0	(2)
Pyridine (technical)	3.68	(2)	29.5
Piperidine	(2)	(2)	(2)
Quinoline, pure	1.64	224.2	17.5
Quinaldine	1.73	(2)	19.6

TABLE D

SOLUBILITY OF CO_2

Solvent	cc. CO_2 (red. to STP) dissolved at 20° and 1 atm. by 1 cc. liquid.
Acetonitrile	5.39
Acetic anhydride	5.12
Methylglycol acetate	5.12
Dimethylsulfate	4.69
Ethylglycol acetate	4.63
Glycol diacetate	4.48
Diethyl oxalate	4.31
Propyl acetate	4.25
n-Butyl acetate	4.19
Ethyl acetate	4.17
Acetyl acetone	4.17
Acetoacetic ester	4.14
Glacial acetic acid	4.13
Ethyl malonate	4.11
Ethyl butyrate	4.02
Isoamyl acetate	4.02
Diethyl malonate	4.0
Propionic acid	3.95
Methyl propionate	3.91
Cyclohexanone	3.84
Pyridine	3.84
Methyl succinate	3.84
Butylglycol acetate	3.77
Ethyl chloroacetate	3.75
Epichlorohydrin	3.72

TABLE I

SOLUBILITY OF SO_2

Solvent	c.c. SO_2 (reduced to S.T.) dissolved at 20° and 1 atm. by 1 cc. of liquid.
Acetone	221.7
Acetonitrile	250.0
Methylglycol acetate	265.8
Formamide	241.9
Acrolein	231.5
Methyl acetate	231.0
Epichlorhydrin	226.5
Methyl ethyl ketone	224.2
Quinoline	224.2
Acetic anhydride	217.6
Glycol diacetate	214.0
Cyclohexanone	211.2
Ethylglycol acetate	208.8
Glycol monoacetate	206.8
Ethyl acetate	197.7
Methanol	197.7
Acetoacetic ester	197.4
Chloroacetone	192.5
Acetylacetone	186.5
Methyl propionate	186.6
Ethyl formate	183.1
Dimethyl sulfate	178.1
Diethyl oxalate	176.5
Furfural	172.0
Diethyl malonate	170.0

TABLE F

SOLUBILITY OF H_2S

Solvent	cc. H_2S (reduced to S.T.P.) dissolved at 20°C. and 1 Atm. by 1 cc. of liquid.
Pyridine	29.5
Methylglycol acetate	24.4
Methylethyl ketone	23.5
Ethylglycol acetate	23.1
Ethyl acetate	20.95
Ethyl propionate	20.80
Acetone	20.55
Acetonitrile	20.28
Propyl acetate	20.20
Methyl propionate	19.7
Butylglycol acetate	19.65
Epichlorhydrin	19.45
Hexamethylenediimine	19.08
Furaldehyde	18.7
n-Butyl acetate	18.6
Quinaldine	18.6
Ethyl oxoformate	18.5
Ethyl butyrate	18.3
Acetonoetic ester	17.95
Glycol diacetate	17.7
Ethyl malonate	17.65
Quinoline	17.5
Bromoform	17.5
Methyl acetate	17.25
Isoamyl acetate	17.25