Part I

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Activity Coefficients as a Function of Structure and Media

N. C. DENO and HENRY E. BERKHEIMER
Pennsylvania State University, University Park, Pa.

The activity coefficient, f, being the free energy per particle (activity/concentration), occupies a unique position in all problems involving equilibria. With the advent of transition state theory, it appears that these same activity coefficients will be the focal point of problems involving the variation of kinetics with solvent.

The most successful approach to the problem of the variation of f with solvent is that of McGowan (*15*), who developed a train of thought initiated by Langmuir. The purpose of the present work was to expand the experimental verification of McGowan's equation:

$$\text{Log } (c_1/c_2) = k_M P \tag{1}$$

UNCHARGED INERT SOLUTES

McGowan (*15*) demonstrated that Equation 1 correlated the partition of an inert uncharged solute between two immiscible liquids. P is the parachor of the solute; c_1 and c_2 are the concentrations (in moles per liter) of the solute in solvents 1 and 2; and k_M is a constant characteristic of the two solvents. McGowan showed that this equation was applicable even when c_1 represented the molar concentration of a liquid in itself; in that event, Equation 1 predicted the solubility in solvent 2.

Because inert uncharged solutes generally obey Henry's law, the relation $\log\ (c_1/c_2) = \log\ (f_2/f_1)$ is valid where f_1 and f_2 are the activity coefficients (activity $= cf$) of the solute in solvents 1 and 2. Equation 1 thus predicts the change in activity coefficient between two media. The great importance of such a relation led to amplifying the experimental test of Equation 1 to solutes possessing a greater variety of sizes and shapes than those originally cited by McGowan (*15*).

The data in Table I show that Equation 1 is generally valid for inert uncharged molecules including those possessing large dipole moments such as the halogen substituted hydrocarbons. When solvent 1 is any solvent giving a nearly ideal solution, and solvent 2 is water, the values of k_M center around 0.0130. The iodo compounds have values of $\log\ (c_1/c_2)/P$ that are consistently too high. This discrepancy would be removed by a larger parachor atomic increment for iodine.

DERIVATION OF EQUATION 1

Equation 1 owes its origin to Langmuir's idea (*13*) that a major factor in solubility relationships was the energy needed to make a hole in the solvent in which to place the solute molecule. This idea was developed by several authors, and these references are given by McGowan (*14*, *15*). McGowan's derivation of Equation 1 is essentially as follows.

The free energy change accompanying the transfer of a particle of solute from solvent 1 to solvent 2 is given by Equation 2. E_{11} and E_{22} are the energies of hole formation in solvents 1 and 2. E_{1-S} and E_{2-S} are the interaction energies between solute, s, and solvents 1 and 2. The absence of any entropy term is based on the presumption that the freedom of motion of solute and solvent will not be inhibited if only nondirectional London dispersion forces are present. Further, the transfer of the particle of solute will be made under the condition that the concentration of solute in each phase is the same so that no entropy difference arises due to changes in concentration.

$$-\Delta F = E_{11} - E_{22} - E_{1-S} + E_{2-S} \tag{2}$$

If $E_{1-S} = E_{2-S}$, Equation 2 simplifies to Equation 3. The success of Equation 1 naturally validates this interesting assumption. Independently, London dispersion forces were found to be insensitive to chemical composition from studies on solubilities of inert gases (*10*, *19*) and from the fact that absorption energies of inert gases were insensitive to the chemical composition of the solid surface (*3*).

It is assumed that the energy required to make the hole is proportional to the volume of the hole and that the solutes volume is the same in both solvents. The parachor is used as the measure of the volume of solute. Equation 4 follows from these assumptions.

$$-\Delta F = E_{11} - E_{22} \tag{3}$$

$$-\Delta F = P(\text{constant}_1 - \text{constant}_2) = P(\text{constant}) \tag{4}$$

If a single standard state is defined for the solute in all phases, ΔF is given by Equation 5. The values of c_1 and c_2 are equal and cancel because of the stipulation that the transfer of solute particle was made at constant concentration. Equations 4 and 5 combine to give Equation 6.

$$\Delta F = RT \ln\ (a_2/a_1) = RT \ln\ (f_2c_2/f_1c_1) = RT \ln\ (f_2/f_1) \tag{5}$$

$$\text{Log } (f_2/f_1) = k_M P \tag{6}$$

Although Equation 6 has been derived for a particular process, all terms in Equation 6 are concentration independent if Henry's law applies. Thus, Equation 6 is valid when solutions of the solute in solvents 1 and 2 are in equilibrium and at equilibrium $f_2/f_1 = c_1/c_2$. Equation 6 thus reduces to Equation 1 and the derivation is complete.

The success of Equation 1 with molecules possessing large

Table I. Data on Solubility of Organic Compounds in Water at 25° C.

Constancy of $(1/p)\log(c_1/c_2)$, thus validity of Equation 1

Hydrocarbon	P^a	$(\text{Log } c_1)^b$	$-(\text{Log } c_2)^b$	$\frac{\text{Log }(c_1/c_2)}{P}$	Ref.
Liquid Aromatic Hydrocarbons					
Benzene	206	1.05	1.64	0.0131	(1, 6, 11)
Toluene	246	0.97	2.19	0.0129	(1, 6, 11)
Ethylbenzene	286	0.91	2.79	0.0129	(1, 6, 11)
1,2-Dimethylbenzene	283	0.91	2.72	0.0128	(1)
1,3-Dimethylbenzene	286	0.91	2.76	0.0128	(1, 6)
1,4-Dimethylbenzene	286	0.91	2.73	0.0127	(1, 6)
Propylbenzene	326	0.86	3.34	0.0129	(1)
			(3.00)	(0.0118)	(11)
Isopropylbenzene	322	0.85	3.22	0.0127	(1)
1,3,5-Trimethylbenzene	324	0.86	3.09	0.0122	(1)
Butylbenzene	366	0.80	3.94[c]	0.0129	(1)
			(3.43)	(0.0116)	(11)
2-Butylbenzene	362	0.81	3.67[c]	0.0124	(1)
tert-Butylbenzene	358	0.81	3.60	0.0123	(1)
tert-Amylbenzene	398	0.77	4.15	0.0124	(1)
2-Octylbenzene[d]	526	0.65	5.80	0.0122	(5)
Diphenylmethane	421	0.78	4.06	0.0115	(1, 5)
1,2,3,4-Tetrahydro-naphthalene	330	0.86	3.49	0.0132	(5)
Styrene	274	0.94	2.54	0.0127	(1)
α-Methylstyrene	310	0.88	3.01	0.0126	(5)
1,1-Diphenylethylene	445	0.76	4.52	0.0119	(1)
			(3.18)	(0.0111)	(1)
2,4-Diphenyl-4-methyl-2-pentene	597	0.62	6.98	0.0127	(5)
Phenylacetylene	264	0.96	2.35	0.0125	(5)
Liquid Aliphatic Hydrocarbons					
Pentane	231	0.94	2.30	0.0140	(18)
Hexane	271	0.88	2.79	0.0135	(18)
Heptane	311	0.84	3.15	0.0128	(18)
Octane	351	0.79	3.91	0.0134	(18)
Octadecane	751	0.48	6.67	0.0095	(4)
Solid Aromatic Hydrocarbons					
		$(\text{Log } c_1)^e$			
1,2,4,5-Tetramethyl-benzene	358	0.34	3.84	0.0117	(5)
Pentamethylbenzene	390	0.44	3.98	0.0113	(5)
Biphenyl	381	0.54	4.46	0.0131	(1, 6)
				(0.0127)[f]	
trans-1,2-Diphenyl-ethylene	446	- 0.31	5.93	0.0126	(1)
Naphthalene	312	0.49	3.57	0.0130	(6)
				(0.0125)[f]	
Acenaphthene	364	0.06	4.40	0.0123	(5)
Pyrene	456	- 0.20	6.09	0.0129	(9)
Triphenylene	525	- 0.75	6.75	0.0114	(9, 11)
Phenanthrene	418	0.31	5.05	0.0128	(9, 11)
				(0.0121)[f]	
Anthracene	418	- 1.04	6.35	0.0127	(9, 11)
Fluoranthene	459	0.07	5.90	0.0130	(9, 11)
Chrysene	524	- 1.54	8.18	0.0127	(9)
			7.56	0.0115	(11)
Benz[a]anthracene	524	- 0.56	7.33	0.0129	(9, 11)
Benz[b]anthracene	524	- 1.77	8.27	0.0124	(9, 11)
Dibenz[a,h]anthracene	630	- 1.93	8.71	0.0108	(9, 11)
Gaseous Hydrocarbons[m]					
		$(\text{Log } h_1)^g$	$-(\text{Log } h_2)^h$	$\frac{\text{Log }(c_1/c_2)^i}{P}$	Ref.
Methane	73	1.70	2.87	0.0160	(18)
				0.0150[l]	(18)
Ethane	111	0.77	2.74	0.0177	(18)
				0.0154[l]	(18)
Propane	151	0.40[j]	2.86	0.0163	(8, 12)
Butane	191	- 0.22[j]	2.95	0.0166	(8, 12)
Ethylene	99	0.92	2.32	0.0141	(18)
				0.0148[l]	(18)
Propene	139	0.09[k]	2.03	0.0140	(18)
Acetylene	90	0.70	1.38	0.0075	(18)

Compound	P^a	$(\text{Log } c_1)^b$	$-(\text{Log } c_2)^b$	$\frac{\text{Log }(c_1/c_2)}{P}$	Ref.
Chlorinated Aliphatic Hydrocarbons					
Chloromethane	113			0.0106[i]	(18)
Dichloromethane	153	1.20	0.63	0.0120	(18)
Trichloromethane	193	1.10	1.21	0.0120	(18)
Tetrachloromethane	233	1.02	2.30	0.0142	(18)
Chloroethane	151	1.15	0.93	0.0138	(18)
1,1-Dichloroethane	191	1.08	1.29	0.0124	(18)
1,2-Dichloroethane	191	1.10	1.06	0.0113	(18)
1,1,1-Trichloroethane	231	1.00	2.01	0.0130	(18)
1,1,2-Trichloroethane	231	1.03	1.48	0.0109	(18)
1,1,1,2-Tetrachloroethane	271	0.98	2.18	0.0117	(18)
1,1,2,2-Tetrachloroethane	271	0.98	2.77	0.0138	(18)
Pentachloroethane	311	0.92	2.64	0.0115	(18)
1-Chloropropane	191	1.05	1.46	0.0132	(18)
2-Chloropropane	191	1.04	1.41	0.0128	(18)
1,2-Dichloropropane	231	1.01	1.61	0.0116	(18)
1,3-Dichloropropane	231	1.02	1.62	0.0116	(18)
1-Chlorobutane	231	0.98	2.16	0.0136	(18)
1-Chloro-2-methylpropane	227	0.97	2.00	0.0131	(18)
2-Chloro-2-methylpropane	227	0.96	2.13	0.0136	(18)
cis-1,2-Dichloroethylene	179	1.12	1.44	0.0143	(18)
trans-1,2-Dichloroethylene	179	1.12	1.19	0.0129	(18)
1,1,2-Trichloroethylene	219	1.05	2.12	0.0145	(18)
Liquid Brominated Aliphatic Hydrocarbons					
Dibromomethane	178	1.16	1.18	0.0131	(18)
Tribromomethane	231	1.06	1.91	0.0129	(18)
Bromoethane	164	1.12	1.08	0.0134	(18)
1,2-Dibromoethane	216	1.06	1.67	0.0126	(18)
1-Chloro-2-bromoethane	204	1.07	1.32	0.0117	(18)
1,1,2,2-Tetrabromoethane	321	0.93	2.73	0.0114	(18)
1-Bromopropane	204	1.04	1.70	0.0134	(18)
2-Bromopropane	204	1.03	1.59	0.0128	(18)
1-Bromobutane	244	0.98	2.36	0.0137	(18)
1-Bromo-2-methylpropane	240	0.96	2.43	0.0141	(18)
Liquid Iodinated Aliphatic Hydrocarbons					
Iodomethane	148	1.21	1.00	0.0149	(18)
Diiodomethane	223	1.09	2.35	0.0154	(18)
Iodoethane	186	1.09	1.60	0.0145	(18)
1-Iodopropane	226	1.01	2.20	0.0142	(18)
2-Iodopropane	226	1.00	2.09	0.0137	(18)
1-Iodobutane	266	0.94	2.94	0.0146	(18)
Liquid Halogenated Aromatic Hydrocarbons					
Fluorobenzene	216	1.03	1.87	0.0134	(1)
Chlorobenzene	246	0.98	2.44	0.0139	(1)
Bromobenzene	259	0.98	2.68	0.0141	(1)
Iodobenzene	281	0.85	3.11	0.0141	(1)
1,2-Dichlorobenzene	282	0.95	3.01	0.0140	(18)
1,3-Dichlorobenzene	286	0.94	3.08	0.0140	(18)

[a] Parachors computed from tabulated parameters (16).

[b] c_1 and c_2 are the concns. in moles/liter of the pure solute in itself (c_1) and of a saturated solution of the solute in water (c_2).

[c] Values estimated by using data in 1 *M* salt solution and making a small correction for salting out. Data listed for the compounds in pure water, probably in error.

[d] Sample furnished by J. A. Dixon, Director of American Petroleum Institute Research Project 42, Pennsylvania State University.

[e] Molar solubilities in benzene or in a few cases toluene, solvents in which the solute forms a nearly ideal solution.

[f] Values computed from the expression $\log(c_1'/c_2')/P$. Log c_1' should be the molar concn. of the supercooled liquid, but as an approximation, the molar concn. of the solid has been used. Log c_2' is the solubility of the supercooled liquid in water. It was calcd. from the relation $\log c_2' = \log c_2 + (L_f/4.58)(1/T - 1/T_m)$, as proposed and explained by McGowan (1).

[g] h_1 is Henry's law constant for the solute in benzene. Units of h_1 are atm. liters/moles.

[h] h_2 is corresponding Henry's law constant in water.

[i] $\text{Log }(c_1/c_2) = \log(h_2/h_1)$.

[j] Solvent 2-propanol instead of benzene.

[k] Solvent xylene instead of benzene.

[l] Calcd. from partition data between benzene and water.

[m] Values of k_M for very small molecules are abnormally high because they partly fit into interstitial space and thus the hole required for them need only be partly generated. This effect is exhibited in these gaseous hydrocarbons.

Table II. Solute-Water Hydrogen Bonding Energies, E_H

Compound	P^a	$(\text{Log } c_1)^a$	$-(\text{Log } c_2)^a$	$E_H{}^b$, Kcal./Mole
Ethers				
Ethyl ether	211	0.98	0.11	2.26
Methyl propyl ether	211	1.00	0.38	1.86
Methyl 2-propyl ether	207	1.00	0.06	2.23
Ethyl propyl ether	251	0.92	0.67	2.30
Ethyl 2-propyl ether	247	0.91	0.56	2.38
Methyl butyl ether	251	0.93	1.00	1.84
Methyl 1-(2-methylpropyl) ether	247	0.92	0.90	1.91
Methyl 2-butyl ether	247	0.93	0.74	2.11
Methyl dimethylethyl ether	243	0.93	0.23	2.74
Propyl ether	291	0.86	1.61	1.80
Propyl 2-propyl ether	287	0.85	1.34	2.11
3-Propenyl ether	268	0.91	1.51	1.45
Methyl phenyl ether	266	0.97	2.97[c]	...[c]
2,2′-Dichlorodiethyl ether	290	0.93	1.13	2.34
1,1′-Dimethyl-2,2′-dichlorodiethyl ether	362	0.81	2.00	2.60
2,2-Dimethyloxacyclopropane	192	1.05	0.12	1.82
Oxacyclohexane	221	1.01	0.03	2.52
Chloromethyloxacyclopropane	192	1.11	0.16	1.69
1-Chloromethyl-1-methyloxacyclopropane	228	1.02	0.55	1.90
Diethoxymethane	271	0.90	0.16	1.81[d]
1,1-Diethoxyethane	307	0.84	0.33	1.93[d]
1,2-Diethoxyethane	311	0.85	0.15	2.08[d]
Tripropoxymethane	487	0.67	0.97	2.14[e]
1,3,5-Trioxacyclohexane	301	0.88	0.14	1.32[e]
			Median value	2.11
Ketones				
2-Pentanone	238	0.98	0.20	2.62
3-Pentanone	238	0.98	0.26	2.54
3-Methyl-2-butanone	234	0.98	0.16	2.60
2-Hexanone	277	0.90	0.78	2.63
3-Methyl-2-pentanone	273	0.90	0.68	2.70
4-Methyl-2-pentanone	273	0.90	0.72	2.64
4-Methyl-3-pentanone	273	0.90	0.82	2.51
4-Methyl-3-pentene-2-one	244	0.94	0.52	2.34
3,3-Dimethyl-2-butanone	269	0.91	0.72	2.56
2-Heptanone	317	0.86	1.44	2.49
4-Heptanone	317	0.85	1.48	2.45
5-Nonanone	394	0.76	2.55	2.49
Menthone	405	0.76	2.35	2.96
Acetophenone	283	0.93	1.34	1.93
			Median value	2.55
Aldehydes				
Butanal	200	1.05	0.28	1.60
Hexanal	280	0.92	1.30	1.95
2-Ethylbutanal	276	0.91	1.52	1.59
2-Ethylhexanal	356	0.81	2.13	2.32
2-Ethyl-2-hexenal	343	0.83	2.46	1.59
Benzaldehyde	254	1.00	1.55	0.85
			Median value	1.59
Esters				
Methyl propionate	215	1.02	0.15	2.23
Ethyl acetate	215	1.01	0.03	2.41
Vinyl acetate	203	1.03	0.64	1.33
Methyl butyrate	255	0.94	0.83	2.12
Ethyl propionate	255	0.94	0.64	2.38
Propyl acetate	255	0.94	0.75	2.23
Isopropyl acetate	251	0.93	0.54	2.45
Ethyl butyrate	295	0.85	1.23	2.41
Propyl propionate	295	0.88	1.34	2.22
Isopropyl propionate	291	0.87	1.29	2.23
Butyl acetate	295	0.88	1.37	2.18
Isobutyl acetate	291	0.87	1.28	2.25
2-Butenyl acetate	279	0.91	0.70	2.77
Ethyl pentanoate	335	0.83	1.74	2.44
Ethyl β-methylbutyrate	331	0.82	1.89	2.18
Propyl butyrate	335	0.83	1.92	2.19
Isopropyl butyrate	331	0.83	1.94	2.10
Butyl propionate	335	0.83	1.87	2.26
Pentyl acetate	335	0.83	1.86	2.27
Esters continued				
Isopentyl acetate	331	0.82	1.91	2.15
Hexyl acetate	375	0.78	2.05	2.81
Pentyl propionate	375	0.78	2.25	2.52
Isopentyl propionate	371	0.78	2.21	2.51
Ethyl heptanoate	415	0.74	2.74	2.63
Pentyl butyrate	415	0.74	2.49	2.97
Ethyl octanoate	455	0.70	3.39	2.49
2-Chloroethyl acetate	255	0.97	0.61	2.37
Ethyl β-phenylpropionate	430	0.75	3.01	2.52
			Median value	2.26
Formate Esters				
Ethyl formate	175	1.10	−0.15	1.82
Propyl formate	215	1.01	0.51	1.75
Isopropyl formate	211	1.00	0.63	1.52
Isobutyl formate	251	0.93	1.00	1.82
Isopentyl formate	291	0.87	1.52	1.90
			Median value	1.82
Aromatic Esters				
Methyl benzoate	310	0.90	1.53	2.19
Ethyl benzoate	350	0.85	2.40	1.78
Ethyl cinnamate	415	0.77	3.09	2.11
Benzyl benzoate	485	0.72	4.13	2.00
			Median value	2.05
Diesters and Triesters				
Dimethyl butanedioate (succinate)	319	0.89	1.21	1.40[d]
Diethyl propanedioate (malonate)	359	0.82	0.90	2.02[d]
Diethyl butanedioate (succinate)	399	0.78	1.00	2.34[d]
Diethyl pentanedioate (glutarate)	439	0.74	1.33	2.48[d]
Diethyl hexanedioate (adipate)	479	0.70	1.68	2.64[d]
Diethyl heptanedioate (pimelate)	519	0.66	2.04	2.78[d]
Diethyl octanedioate (suberate)	559	0.63	2.53	2.82[d]
Diethyl nonanedioate (azelate)	599	0.61	2.99	2.87[d]
Diethyl decanedioate (sebacate)	639	0.57	3.51	2.90[d]
Glyceryl triacetate	458	0.73	0.51	2.15[e]
Dimethyl phthalate	414	0.79	1.69	1.99[d]
Diethyl phthalate	494	0.70	2.57	2.16[d]
Dibutyl phthalate	654	0.58	4.40	2.41[d]
			Median value	2.41
Nitriles				
Acetonitrile	122			2.48[f]
Butyronitrile	200			2.20[f]
Succinonitrile	212			2.16[d,f]
Nitroalkanes				
Nitroethane	169	1.15	0.24	1.11
1-Nitropropane	209	1.05	0.81	1.18
2-Nitropropane	205	1.06	0.73	1.19
Nitroaromatics				
Nitrobenzene	264	1.01	1.80	0.85
4-Chloronitrobenzene	304			−0.18[g]
2-Nitrotoluene	298	0.93	2.32	0.85
3-Nitrotoluene	299	0.93	2.44	0.71
2,4-Dinitrotoluene	362			0.98[d]
2,4,6-Trinitrotoluene	420			0.81[d]
2,4,6-Trinitrochlorobenzene	420			0.98[e]
			Median value	0.85
Miscellaneous				
Acetic anhydride	159	1.03	0.06	1.34
Acetyl fluoride	112	1.21	0.10	0.21
Diethyl sulfide	240	0.97	1.45	0.96
2,2′-Dichlorodiethyl sulfide	320	0.90	2.36	1.23
Ethanethiol	160	1.13	0.60	0.48

[a] Cf. *a*, Table I. Solubility data mainly from (*2* and *18*). [b] $E_H = 1.37 E_A$ and E_A calcd. from Eq. 7. $k_M = 0.0130$ used throughout. [c] An error probably made in power of 10; 0.97 would give 2.08, reasonable for E_H. [d,e] To get E_H per functional group, value calcd. from Eq. 7 was divided by [d] 2, [e] 3. [f,g] Calcd. using $\log(c_1/c_2)$ = [f] $(c_{\text{ether}}/c_{\text{water}})$, [g] $(c_{\text{benzene}}/c_{\text{water}})$.

dipole moments (cf. the halogen compounds in Table I) is partly due to the fact that dipole-induced dipole forces are small, and that the energy of the dipole-dipole interaction in pure solute compensates for the dipole-dipole interaction between solute and solvent. This compensation does not arise when Equation 1 is used for data on the distribution of a solute with large dipole between a solvent with large dipole and a solvent with no dipole. In such cases we may anticipate that the data on halogenated hydrocarbons will not give as constant a k_M, nor will it be the same k_M value as with hydrocarbons.

A troublesome point in the derivation is whether the energy required to make the hole is a function of the volume or surface area of the hole. Langmuir (*13*) considered it to be a function of the area, but Equation 1 assumes it to be proportional to the volume. There was some question in McGowan's paper (*15*), whether Equation 1 had been tested with solutes of sufficiently different area to volume ratios to distinguish an area or a volume dependence. The agreement of the data in Table I with Equation 1 clearly seems to indicate a volume dependence.

Eley (*10*) computed the energy of making a hole on three different bases. If a solvent is considered to be composed of cubes, and the cohesive energy is obtained by faces of cubes being in contact, two of Eley's three methods do not seem proper for the problem. The compressibility which was the basis for the first method, measures the energy required to compress the cubes or perhaps reduce interstitial space formed by molecular motion.

The heat of vaporization, the basis for Eley's third method, is not applicable because the removal of a single cube destroys 6 faces of contact, whereas the removal of two adjacent cubes (to create a hole for a solute particle twice the size of a solvent particle) destroys only 10/2 or 5 faces of contact per volume of solvent particle.

The surface energy, which is the basis for Eley's second method, seems reasonable but leads to an area rather than the volume dependence required by Equation 1.

HYDROGEN-BONDED SOLUTES

McGowan found that by adding a constant to Equation 1 to give Equation 7, the theory could be extended to solutes that hydrogen-bond. Equation 7 can be derived from Equation 2 in a manner similar to the derivation of Equation 1 if a term is added to Equation 2 which represents the difference in orbital overlap energy of solute to solvents 1 and 2. The derivation is not as satisfactory because the presence of chemical bonds will certainly restrict solvent motion and introduce an entropy effect.

For the case where c_1 is the molar concentration of liquid solute and c_2 is the molar solubility in water, McGowan found fair agreement if $E_A = 1.75$ in Equation 7. However, the agreement is not as good as indicated by McGowan because only a portion of the literature data was used.

$$\text{Log } (c_1/c_2) = k_M P - E_A \tag{7}$$

It was decided to test Equation 7 more thoroughly and to separate the compounds into their respective functional groups as shown in Table II. The values of E_A from Equation 7 have been converted to the hydrogen bond energy, E_H, in kilocalories per mole by multiplying by 2.3 RT which is 1.37 at 25°.

The most notable fact about the value of E_H in Table II is that for a particular functional group, systematic trends with structure are virtually absent. This fact renders suspect the values of E_H which deviate very far from the median values, and in these cases, solubility data will be reinvestigated. Also the median values of E_H are comparable for different functional groups, but there does seem to be enough difference, particularly with nitro compounds, to justify treating the different functional group series separately. The fact that the E_H for nitro compounds is less than for other oxygen-containing functional groups correlates with the lower basicity of the nitro group.

SOLUBILITIES IN LIQUID SULFUR DIOXIDE

The data in Table III show that Equation 1 correlates the solubilities of saturated hydrocarbons in liquid sulfur dioxide. The value of k_M for liquid hydrocarbon–liquid sulfur dioxide is 0.0030 at -29° C. This result can be used along with data on the partition of aromatic hydrocarbons between liquid hydrocarbon and liquid sulfur dioxide to evaluate the bonding energy of aromatic hydrocarbon to sulfur dioxide. Although the data are limited to only four benzene derivatives, the results in Table IV show E to be about 1.7 kcal. per mole.

The partition between liquid hydrocarbon, H, and liquid sulfur dioxide, SO_2, can be calculated at -29° C. for any saturated hydrocarbon by Equation 8 and for any aromatic hydrocarbon by Equation 9 [the term 1.49 in Equation 9 is ($E/2.30\,RT$)].

$$\text{Log } (c_H/c_{SO_2}) = 0.0030\ P \tag{8}$$

$$\text{Log } (c_H/c_{SO_2}) = 0.0030\ P - 1.49 \tag{9}$$

SOLUBILITIES IN LIQUID AMMONIA

Equation 1 correlates the solubilities of saturated hydrocarbons in liquid ammonia (Table V). The value of k_M for liquid hydrocarbon–liquid ammonia is 0.0044 at 25° C. and 0.0109 at -33.3° C. (boiling point of ammonia).

Surprisingly, the data for olefins in Table VI did not fit Equation 1. The deviation was interpreted as a bonding energy, E, between the olefin and ammonia. Further work will be necessary to determine whether it is really a bonding energy or the theory presented in this article needs modification. This apparent bonding energy is relatively constant at 0.67 kcal. per mole per double bond at -33.3° C. Dienes have values of E twice that of mono-olefins. The value of E for aromatics is three

Table III. Data on Solubility of Alkanes in Liquid Sulfur Dioxide at –29° C.

(Constancy of $(1/p)$ Log_1 (c_2/c), thus Validity of Equation 1)

Alkane	P^a	$(\text{Log } c_1)^b$	$-(\text{Log } c_2)^c$	$(1/P)$ Log (c_1/c^2)
Butane	191	1.02	– 0.38	0.0033
Hexane	271	0.89	0.01	0.0030
Heptane	311	0.85	0.30	0.0027
Nonane	391	0.75	0.60	0.0029
Decane	431	0.72	0.99	0.0025

[a] cf. *a*, Table I.

[b] Concentration in moles per liter of the pure alkane at -29° C.

[c] Solubility of the alkane in liquid sulfur dioxide at -29° C. in the units moles per liter (*17*).

Table IV. Calculation of the Bonding Energy, *E*, Between Aromatic Hydrocarbons and Liquid Sulfur Dioxide at –29° C.

Hydrocarbon	P^a	Log $(c_H/c_{SO_2})^b$	E^c (kcal./mole)
Benzene	206	– 0.70	1.46
Toluene	246	– 0.72	1.62
Xylene[d]	286	– 0.71	1.74
2-Butylbenzene	366	– 0.43	1.70

[a] cf. *a*, Table I.

[b] c_H and c_{SO_2} are the solubilities in moles per liter in the alkane, H, and in liquid sulfur dioxide (SO_2). The hydrocarbon, H, varied. For toluene it was heptane, for xylene it was nonane, and for 2-butylbenzene it was decane. The value of c_H is probably insensitive to the alkane used. For example, with benzene, c_H was -0.70 for butane, -0.77 for hexane, -0.70 for cyclohexane, -0.69 for heptane, and -0.78 for decane. With benzene, the median value of c_H was used. All exptl. data obtained from (*17*).

[c] E was calculated from log $(c_H/c_{SO_2}) = 0.0030\ P - E/2.30\ RT$, an adaptation of Eq. 7.

[d] The xylene was a mixture containing 50% *m*, 25% *p*, and 25% *o*.

times the value for mono-olefins which could be regarded as due to three double bonds in the benzene ring, but may also be just coincidence. The values of E for styrene and indene are between three and four times the value for mono-olefins. Regardless of the interpretation of E, it can be treated as a bonding energy, and the solubility at −33.3° C. in liquid ammonia can be calculated by Equation 10 for saturated hydrocarbons, by Equation 11 for unsaturated hydrocarbons where N is the number of unsaturated linkages, and by Equation 12 for benzene with saturated substituents.

$$\text{Log }(c_1/c_2) = 0.0109\ P \tag{10}$$

$$\text{Log }(c_1/c_2) = 0.0109\ P - 0.67\ N/2.30\ RT \tag{11}$$

$$\text{Log }(c_1/c_2) = 0.0109\ P - 1.85/2.30\ RT \tag{12}$$

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Table V. Data on Solubility of Saturated Hydrocarbons in Liquid Ammonia at 25° C.

(Constancy of $(1/p)$ Log(c_1/c_2), thus validity of Equation 1)

Hydrocarbon	P[a]	(Log c_1)[b]	−(Log c_2)[c]	$\frac{\text{Log }(c_1/c_2) \times 10^4}{P}$
Butane	191	1.00	0.13	46
Pentane	231	0.94	0.08	44
2-Methylbutane	227	0.93	0.04	43
Hexane	271	0.88	0.35	45
2-Methylpentane	267	0.88	0.30	44
3-Methylpentane	267	0.89	0.27	43
2,2-Dimethylbutane	263	0.87	0.27	44
2,3-Dimethylbutane	263	0.88	0.31	46
Heptane	311	0.84	0.62	47
Octane	351	0.79	0.98	50
2,2,4-Trimethylpentane	339	0.78	0.75	45
Nonane	391	0.75	1.21	50
Decane	431	0.71	1.34	48
3,3,5-Trimethylheptane	419	0.72	1.02	42
2,2,3,4-Tetramethylhexane	415	0.72	1.02	42
Cyclopentane	203	1.03	−0.07	47
Cyclohexane	241	0.96	0.20	48
Methylcyclopentane	239	0.95	0.16	46
Methylcyclohexane	277	0.89	0.34	44
Ethylcyclopentane	279	0.89	0.42	47
Ethylcyclohexane	317	0.84	0.58	45
2-Propylcyclopentane	315	0.84	0.55	44
2-Butylcyclopentane	355	0.79	0.76	44
Decahydronaphthalene	363	(0.80)[d]	1.03	50
Pentyldecahydronaphthalene[e]	559	(0.62)[d]	1.86	44
Tris-(2-propyl)cyclohexane[e]	577	(0.60)[d]	1.63	39
Methyl-tris-(2-propyl)-cyclohexane[e]	613	(0.57)[d]	2.04	43
Diethyl-bis-(2-propyl)-cyclohexane[e]	617	(0.57)[a]	1.74	38

[a] cf. *a*, Table I.
[b] Concentration, moles per liter, pure alkane at 25° C.
[c] The solubility of the alkane in liquid ammonia at 25° C. in the units moles per liter. These solubilities were calculated from data obtained by the Petroleum Refining Laboratory under the direction of Fenske at the Pennsylvania State University. Data are summarized (7). The solubility data were measured in solutions that were 1–10% by weight. To obtain data at 25° C. it was sometimes necessary to extrapolate the data. Use was made of the fact that plots of log of the % by weight against temperature^{-1} were linear.
[d] Estimated from data on analogous compounds.
[e] Commercial samples, the positions of the substituents were not known. In the case of the pentyl substituent, the extent of branching in the substituent is not known.

Table VI. Calculation of the Bonding Energy, *E*, between Unsaturated Hydrocarbons and Liquid Ammonia at −33.3° C.

Hydrocarbon	P[a]	(Log c_1^b)	−(Log c_2^c)	E[d]
1-Butene	179	1.03	0.31	0.67
cis-2-Butene	178	1.05	0.28	0.67
trans-2-Butene	178	1.04	0.38	0.57
2-Methylpropene	175	1.03	0.23	0.71
1-Pentene	219	0.97	0.74	0.74
2-Pentene	218	0.98	0.82	0.64
2-Methyl-1-butene	216	0.98	0.70	0.73
2-Methyl-2-butene	215	0.98	0.79	0.63
Cyclohexene	228	1.00	0.95	0.59
4-Methylcyclohexene	264	0.93	1.10	0.93
1-Octene	339	0.81	2.36	0.58
2-Octene	338	0.81	2.40	0.52
2,4,4-Trimethyl-2-pentene	326	0.80	1.95	0.89
3,5,5-Trimethyl-2-heptene	406	0.74	2.17	1.66
3,4,5,5-Tetramethyl-2-hexene	402	0.74	2.17	1.61
			Median value	0.67
1,3-Butadiene	167	1.07	−0.51	1.38
1,3-Pentadiene	167	1.07	0.00	1.36
2-Methyl-1,3-butadiene	203	1.01	0.00	1.31
2-Methyl-1,3-pentadiene	242	0.95	0.51	1.29
1-Methyl-1,3-cyclohexadiene	251	0.95	0.63	1.27
			Median value	1.31
Toluene	246	0.98	−0.01	1.87
Ethylbenzene	286	0.92	0.54	1.82
1,2-Dimethylbenzene	283	0.93	0.56	1.74
1,3-Dimethylbenzene	286	0.93	0.61	1.73
Propylbenzene	326	0.86	0.90	1.97
2-Propylbenzene	322	0.86	0.84	1.98
1,2,4-Trimethylbenzene	322	0.87	0.98	1.82
Indan	295	0.92	0.73	1.72
1-Methyl-4-(2′-propyl)benzene	362	0.81	1.17	2.16
1,2,3,4-Tetrahydronaphthalene	330	0.87	0.93	1.97
Tris-(2-propyl)benzene[e]	554	0.68	1.99	(3.69)
Diethyl-bis-(2-propyl)benzene[e]	595	0.65	2.48	(3.58)
Dipentylbenzene[e]	606	0.65	3.21	(3.01)
			Median value	1.85
Styrene	274	0.95	−0.03	2.26
Indene	282	0.94	0.29	2.02
Pentylnaphthalene[e]	512	0.69	2.52	2.60

[a] cf. *a*, Table I.
[b] Concentration, moles per liter, pure hydrocarbon at −33° C.
[c] The solubility of the hydrocarbon in liquid ammonia at −33° C. (b.p. of ammonia) in the units moles per liter. Solubilities calculated from (7). Extrapolations were sometimes necessary to get data at −33° C.
[d] E was calculated from log $(c_1/c_2) = 0.0109P - E/2.30\ RT$ which is an adaptation of Eq. 7. The value of k_M of 0.0109 was obtained from data on the saturated hydrocarbons which was extrapolated to −33.3° C. (7).
[e] Commercial samples, the position of the substituents are unknown. Also the degree of branching in the pentyl substituent is unknown. These circumstances plus the fact that the values of E for these compounds are far out of line renders the solubility data suspect.