[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Solubilities of Standard Solid Solutes in Fluorochemicals

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The solubilities of three "standard" solutes, iodine, stannic iodide and phenanthrene in a perfluoroamine, $(C_4F_9)_3N$, and a perfluoroether, $C_8F_{16}O$, were measured at 25, 35 and 45°. The very low solubilities of iodine and stannic iodide, determined by coulometric analysis, were found to fall within the framework of regular solution theory using a low solubility parameter, typical of most fluorochemicals, of 5.7 for both solvents. Phenanthrene solubility, determined spectrophotometrically, was found to be abnormally low. These results are compared with previous data on similar systems from which identical conclusions may be drawn. Only for mixtures of fluorochemicals with substances containing hydrocarbon groups does the regular solution solubility parameter treatment seem definitely inadequate; even there it accounts for the greater part of the non-ideality.

Introduction

The solubility of a component of a solution of non-polar non-electrolytes may frequently be explained with the aid of the simple "regular solution" equation[1]

$$\ln \gamma_2 = \ln (a_2/x_2) = \tilde{V}_2(\delta_1 - \delta_2)^2\phi_1^2/RT \qquad (1)$$

where γ_2 is the activity coefficient of component 2; a_2, its activity; x_2, its mole fraction; and $\tilde{V}_2$, its molar volume (as supercooled liquid); ϕ_1 is the volume fraction of component 1; δ_1 and δ_2 are the "solubility parameters" of the two pure liquids. This solubility parameter is not an arbitrary number, but a definite thermodynamic property of the liquid, the square root of its internal pressure or cohesive energy density, evaluated from its heat of vaporization and its molar volume, and consequently a direct measure of intermolecular forces.

In 1948, Scott[2] concluded that the unusually low solubilities of fluorocarbons in typical organic solvents were a direct result of their low solubility parameters (*ca.* 5.7–6.0 cal.$^{1/2}$ cm.$^{-3/2}$) in agreement with regular solution theory. The meager experimental evidence available at that time seemed to support this point of view.

Since 1948, the miscibilities of several fluorocarbon–hydrocarbon pairs have been studied[3-7] and abnormally low mutual solubilities have been found, in disagreement with the values predicted from the solubility parameters. In an attempt to explain this anomaly, Simons and Dunlap[3] have suggested an "interpenetration" model in which the C–H groups of adjacent hydrocarbon molecules are allowed abnormally close interaction, which leads to a heat of mixing greater than that calculated from the δ-values.

Hildebrand,[8] taking note of the solvent powers of hydrocarbons, has made an alternative suggestion, that their solubility parameters be empirically assigned values about 0.6 unit higher than those calculated from their energies of vaporization per ml. These two proposals are mutually exclusive.[9] Simons and Dunlap's interpenetration model predicts that the hydrocarbons will have abnormally low solvent power for all non-polar substances except other hydrocarbons, while Hildebrand's suggestion requires that they have enhanced solvent power for substances of higher solubility parameter.

Hildebrand[10,11] has shown that solubility data can be compared for self-consistency by comparing $(\delta_1 - \delta_2)$ derived, with the aid of equation 1, from experimental measurements on a series of standard solid solutes in various solvents. If all the δ-differences can be reconciled with a single value, δ_1, for the solvent, the data are self-consistent. If the δ_1-value agrees with that calculated from the heat of vaporization, then it is further substantiated; if not, it may still be expected that solubilities other than those determined will fit this empirical δ_1.

When such a method is applied to fluorochemical solutions, we should be able to obtain information on several points, *e.g.*, (a) how well do the δ-values calculated from solubilities agree with those calculated from the properties of the pure solvent?; (b) do certain solutes have anomalous solubilities leading to a δ_1-value for the fluorochemical solvent not in conformity with that established by other solutes or by the energy of vaporization per ml.? As a start in a general research program on fluorochemical solutions, we chose to measure the solubilities of three such standard solutes, *viz.*, iodine, stannic iodide and phenanthrene in two fluorochemical solvents, a perfluoroamine and a perfluoroether.

Experimental

Materials and Purification.—Perfluoro-tri-*n*-butylamine, $(C_4F_9)_3N$, and a cyclic ether, perfluoro-*n*-propylpyran, $C_8F_{16}O$, both obtained from the Minnesota Mining and Manufacturing Co., were redistilled in an 8 mm. × 91 cm. helipak column (90 plates at total reflux) at a 20:1 take-off ratio. The fraction of the amine boiling from 176–177° and of the ether from 100–101° at 755 mm. were used in the investigation.

Baker and Adamson reagent grade iodine was further purified by resublimation and kept in a desiccator over Drierite.

Eastman Kodak White Label phenanthrene was recrystallized five times from ethanol and the fraction finally retained exhibited a melting point of 101°.

A. D. Mackay, Inc., C.P. stannic iodide was recrystallized five times from chloroform, dried under vacuum, and kept in a vacuum desiccator. This purified sample gave a melting point of 144.5°.

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[1] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," 3rd Edition, Reinhold Publ. Corp., New York, N. Y., 1950.

[2] R. L. Scott, THIS JOURNAL, **70**, 4090 (1948).

[3] J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

[4] J. H. Hildebrand, B. B. Fisher and H. A. Benesi, THIS JOURNAL, **72**, 4348 (1950).

[5] J. H. Simons and J. W. Masteller, *J. Chem. Phys.*, **20**, 1516 (1952).

[6] J. H. Simons and M. J. Linevsky, THIS JOURNAL, **74**, 4750 (1952).

[7] G. J. Rotariu, R. J. Hanrahan and R. E. Fruin, *ibid.*, **76**, 3752 (1954).

[8] J. H. Hildebrand, *J. Chem. Phys.*, **18**, 1337 (1950).

[9] R. L. Scott, *J. Chem. Ed.*, **30**, 542 (1953).

[10] J. H. Hildebrand, *Chem. Revs.*, **44**, 37 (1949).

[11] J. H. Hildebrand and R. L. Scott, ref. 1, Chapter XVII.

TABLE I

SOLUBILITIES IN $(C_4F_9)_3N$ AND $C_8F_{16}O$

		25.0°			35.0°			45.0°		
Solute	Solvent	G./1000 g. solvent	Mole %	γ	G./1000 g. solvent	Mole %	γ	G./1000 g. solvent	Mole %	γ
I_2	Ideal		25.8	1		31.5	1		37.04	1
	$(C_4F_9)_3N$	0.0879	0.0232	1120	0.1440	0.0382	825	0.2556	0.0673	550
		.0881			.1447			.2532		
	$C_8F_{16}O$	.127	.0208	1240	.2071	.0341	924	.3724	0.0615	602
		.126			.2089			.3774		
		.127								
	n-C_7F_{16}	.119	.0182	1400	.0187	.0286	1100			
SnI_4	Ideal		14.6	1		18.2	1		22.3	1
	$(C_4F_9)_3N$	.0104	0.00115	12700	.0200	0.00210	8650	.0395	0.00421	5297
		.0100			.0193			.0393		
	$C_8F_{16}O$	.0216	0.00146	10000	.0361	0.00241	7530	.0737	0.0049	4600
		.0224			.0364			±0.0024 (7 det.)		
$C_{14}H_{10}$	Ideal		22.1	1		28.1	1		36.3	1
	$(C_4F_9)_3N$	.0781	0.0292	757	.1303	0.0489	575	.2010	0.0778	467
		.0771			.1291			.2122		
	$C_8F_{16}O$	.1066	0.0250	884	.1795	0.0415	677	.3026	0.0722	502
		.1076			.1760			.3158		

Apparatus.—A special solubility flask, somewhat similar to that of Hildebrand and Jenks,[12] was devised so that the minute particles of excess solute floating or suspended in the dense fluorochemical solvent would be excluded from the sample taken for analysis, and that loss of solution by volatilization during separation and transfer would be avoided. Moreover, the apparatus makes unnecessary the use of volume or weight pipets, which proved to be somewhat unsatisfactory due to the low surface tension of the fluorochemicals. With the flask held vertical during agitation, solution could not reach the sintered glass disk in the outlet arm. In order to withdraw a sample, the top of the flask was raised slightly above the water level of the bath, the ground glass stopper in the outlet arm removed, and a delivery tube with a jacket through which water from the bath circulated, was inserted. The entire glass assembly was then reimmersed and, after temperature equilibrium was established, it was tilted so that the outlet tube was in a nearly vertical position. Samples of saturated solution were forced through the sintered glass disk and delivery tube into a weighed receiver by blowing calcium chloride-dried air in through a side-arm.

Procedure.—Saturated solutions were prepared by adding an excess of solute to the fluorochemical solvent, keeping it for four days at a temperature about 20° higher than that desired, and then transferring the solution to the special solubility flask immersed in a constant temperature bath of 25, 35, 45°, each maintained at ±0.02°. The immersed flask was agitated for a period of three hours or more to assure complete saturation.

Iodine solutions were delivered into weighed receivers containing a known amount of arsenious oxide in aqueous solution. The amount of iodine initially present was determined by measuring the remaining arsenious oxide with a secondary coulometric titration using electrolytically generated iodine and an amperometric end-point.[13]

Stannic iodide solutions were delivered into a receiver and weighed. A solution of sodium bromide and hydrogen chloride was then added and the iodide titrated coulometrically with electrolytically generated bromine to an iodine monobromide end-point determined amperometrically.[14] Blanks were run on the reagents and small known amounts of stannic iodide in tetrachloromethane were successfully titrated by the method, permitting the conclusion that extraction of the iodine is complete. Despite the precautions taken, there was some (1–10% depending on the time elapsed before measurement) decomposition of the stannic iodide into iodine during the delivery from the solubility vessel. This was corrected for, by extrapolation of the initial coulometric indicator current to zero.[15]

The phenanthrene was determined spectrophotometrically on a Cary Model 11S recording spectrophotometer, using 1-cm. quartz cells. The samples forced through the delivery tube were weighed and diluted tenfold by weight before measurement of the optical density. Extinction coefficients were determined for several absorption peaks by weighing samples of phenanthrene on a microbalance and dissolving in a known weight of fluorochemical. The solubilities were calculated from the absorption peak at 270 mμ for which the extinction coefficients were found to be 1.20×10^4 and 1.15×10^4 l. mole^{-1} cm.$^{-1}$ in $(C_4F_9)_3N$ and $C_8F_{16}O$, respectively.

Results

Table I summarizes the solubility measurements. Included for comparison is the solubility of iodine in perfluoro-n-heptane measured by Hildebrand, Benesi and Mower.[16]

The activity of the solute in a saturated solution is equal to that of the pure solid solute with which it is in equilibrium. This is expressed conventionally as x_2^i, the mole fraction of solute in a saturated ideal solution ($\gamma_2 = 1$). In the non-ideal solution, then, the activity coefficient, γ_2, equals x_2^i/x_2. The ideal solubilities and the activity coefficients in the non-ideal solutions are included in Table I.

Equation 1 permits us to calculate, from the experimentally measured activity coefficients, the difference ($\delta_1 - \delta_2$) of the solubility parameters of solute and solvent and, if the δ_2 is known for the solute, to evaluate an "empirical" δ_1 for the solvent.

As an alternative to the regular solution equation 1, we may instead use the Flory–Huggins[11] equation for the entropy of mixing and write for $\ln \gamma_2$

$$\ln \gamma_2 = \ln (\phi_2/x_2) + (1 - \bar{V}_2/\bar{V}_1)\phi_1 + \bar{V}_2(\delta_1 - \delta_2)^2\phi_1^2/RT \quad (2)$$

This equation corrects (actually overcorrects) for the difference in molecular size of the two components. ϕ_2 is the volume fraction of the solute, computed with the aid of the molar volumes $\bar{V}_1$ and $\bar{V}_2$ of solvent and solute, respectively.

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[12] J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2180 (1920).

[13] W. J. Ramsey, P. S. Farrington and E. H. Swift, *Anal. Chem.*, **22**, 232 (1950).

[14] W. S. Wooster, P. S. Farrington and E. H. Swift, *ibid.*, **21**, 1457 (1949).

[15] Reference 14, Method B.

[16] J. H. Hildebrand, H. A. Benesi and L. M. Mower, THIS JOURNAL, **72**, 1017 (1950).

Table II summarizes the calculations of empirical solubility parameters for the solvents, using equations 1 and 2.

TABLE II

SOLUBILITY PARAMETERS AT 25.0°

Solvent	Solute	$\bar{V}_2$	δ_2	Equation 1 $(\delta_2 - \delta_1)$	Equation 1 δ_1	Equation 2 $(\delta_2 - \delta_1)'$	Equation 2 δ_1'
$(C_4F_9)_3N$	I_2	59	14.1	8.4	5.7	9.0	5.1
	SnI_4	151	11.7	6.1	5.6	6.2	5.5
	$C_{14}H_{10}$	158	9.8	5.0	4.8	5.1	4.7
$C_8F_{16}O$	I_2	59	14.1	8.5	5.6	8.8	5.3
	SnI_4	151	11.7	6.0	5.7	6.0	5.7
	$C_{14}H_{10}$	158	9.8	5.0	4.8	5.1	4.7

Discussion

Aliphatic and cyclic fluorocarbons, in general, have δ-values between 5.5 and 6.0.[2] There is no reason to expect that fluorocarbon derivatives such as $(C_4F_9)_3N$ and $C_8F_{16}O$ would be different since their dipoles are small and "buried," and constitute a very small part of the total molecule. This conclusion is confirmed by data on a series of perfluoro tertiary amines. Rotariu[7] used crude vapor pressure measurements furnished by the manufacturer[17] to calculate δ-values of 6.0, 5.9, 5.9 and 6.8 for $(C_2F_5)_3N$, $(C_2F_5)_2(C_3F_7)N$, $(C_3F_7)_3N$ and $(C_4F_9)_3N$, respectively. This last discordant value, he revised to 5.9 after redetermining the vapor pressure of $(C_4F_9)_3N$ at 25°.

Before comparing these values with those determined from solubility data, we should note that, because of the approximations involved in the theory, agreement is never exact (or if it is, it is fortuitous). In many systems previously investigated, discrepancies of 0.2–0.3 δ-units are not uncommon and better agreement should not be expected.[10] However, a discrepancy which is distinctly larger than this must be taken as an indication of really anomalous behavior.

The empirical solubility parameters (Table II) calculated from iodine and stannic iodide solutions (5.6–5.7) are self-consistent and are in substantial agreement with those calculated from the heat of vaporization. The value derived from phenanthrene solubility, 4.8 for both solvents, is in disagreement with the others but appears to follow the pattern of the abnormally low solubilities previously reported[3-7] for fluorochemical-hydrocarbon pairs; moreover, it is in good agreement with the value of about 5.0 calculated by Rotariu[7] from solubilities in hydrocarbon–$(C_4F_9)_3N$ systems. The δ_1'-values, calculated from the Flory–Huggins equation 2, are not appreciably different and so fail to throw light on the anomaly.

Hildebrand[10] has shown that a solubility parameter $\delta = 9.8$ for phenanthrene (a value consistent with the thermodynamic properties, and the one which we have used) gives excellent agreement with the solubility in carbon tetrachloride, *n*-hexane and diethyl ether. Carbon tetrachloride is one of the most "normal" solvents available, and its solutions consistently agree with solubility parameter predictions.

If "interpenetration" is an important property of the phenanthrene, as Simons has suggested, this would manifest itself in an abnormally low solubility in the non-hydrocarbon carbon tetrachloride, which is not observed. On the other hand, we cannot adopt Hildebrand's suggestion that we arbitrarily increase the solubility parameters of hydrocarbons; a δ of 10.8 for phenanthrene would explain its solubility in fluorochemicals but simultaneously create anomalies in other solvents, particularly carbon tetrachloride.

In a recent paper, Simons and Linevsky[6] report measurements of the solubility of naphthalene, *p*-nitrotoluene and hexachloroethane in two fluorocarbon derivatives, $(C_4F_9)_2O$ and $(C_3F_7)_3N$. They attribute the extremely low solubilities of the first two solutes (less than 1% of the "ideal solubility") to the "interpenetration" effect.[3] However, since solubilities in fluorochemicals are low even in the absence of any special effects, such a conclusion should not be drawn without first comparing the results with solubility parameter theory as we have done above for our measurements.

For napthalene at 25°, δ_2 and $\tilde{V}_2$ are reasonably accurately known and give a consistent picture of its solubility in most non-polar solvents.[10,18] For the other two solutes, we have made estimates based upon fragmentary data and analogous compounds (Table III).

TABLE III

THERMODYNAMIC CONSTANTS AT 25°

	$C_{10}H_8$	$C_7H_7NO_2$	C_2Cl_6
$\tilde{V}_2$(cm.^{3} mole^{-1})	123	120	
δ_2(cal.$^{1/2}$cm.$^{-3/2}$)	9.9	10.3 ± 0.2[a]	9.0 ± 0.4

[a] Estimated by analogy with nitrobenzene and its critical solution temperature with paraffins. See Ref. 1, p. 261.

Table IV shows the computed δ_1's for the fluorocarbon derivatives. The ideal solubility of C_2Cl_6 has been recalculated since Simons and Linevsky failed to allow correctly[19] for the transition at 71° (ΔH^T = 1900 cal.[20]), merely adding ΔH^T to ΔH^F (2400 cal.) at the melting point, 187°.

TABLE IV

SOLUBILITIES AT 25°

Solvent	Solute	x_2	x_2^i	γ_2	$\delta_2 - \delta_1$	δ_1
$(C_4F_9)_2O$	$C_{10}H_8$	0.00257	0.299	177	4.9	5.0
	$C_7H_7NO_2$	.00268	.571	213	5.1	5.2
	C_2Cl_6	.00901	.156	17.3	3.5	5.5
$(C_3F_7)_3N$	$C_{10}H_8$	.00300	.299	100	4.7	5.2
	$C_7H_7NO_2$	.00323	.571	177	5.0	5.3
	C_2Cl_6	.0111	.156	14.1	3.4	5.6

The "thermodynamic" δ-values (from heats of vaporization) for these solvents must lie between 5.7 and 6.0 (Rotariu[7] gives 5.9 for $(C_3F_7)_3N$). The empirical values from the solubility of hexachloroethane are slightly lower (5.5 and 5.6) but the discrepancy lies well within the limits of error expected for the solution theory and our estimate of δ_2. The values for *p*-nitrotoluene are distinctly low

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[17] These compounds, plus the data, are available from the Minnesota Mining and Manufacturing Co., St. Paul 6, Minnesota.

[18] G. Scatchard, *Chem. Revs.*, **8**, 329 (1931).

[19] For the proper treatment of a similar case (*n*-dotriacontane) see J. H. Hildebrand and A. Wachter, *J. Phys. Colloid Chem.*, **53**, 886 (1949).

[20] K. J. Ivin and F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947).

but, by itself, this offers no conclusive evidence for an anomalous fluorocarbon–hydrocarbon interaction, since the effect of the polar nitro group cannot be assessed.

For the naphthalene solutions, the situation is much clearer. To fit the solubility data, we must assign δ_1-values around 5.0, in substantial agreement with our own measurements on phenanthrene solutions. While it is true that the thermodynamic solubility parameters will account for the greater part of the non-ideality (expressed as excess free energy, *i.e.*, log γ, it accounts for 60–80% of the total), the remaining discrepancy is clearly beyond any reasonable estimate of errors. The source of this discrepancy remains to be elucidated.

The conclusion that the generally poor solvent power of the fluorochemicals is primarily due to their low cohesive energy density remains valid. Only for mixtures of fluorochemicals with compounds containing hydrocarbon groups does any further interpretation seem necessary. Moreover, we must emphasize that the fact that the solubility of a substance is very low or differs very greatly from the ideal solubility is no criterion by which to measure the abnormality. Witness our data for stannic iodide in $(C_4F_9)_3N$ in which the solubility is only 0.00001 mole fraction at 25° and for which the activity coefficient exceeds 12,000. Yet, on the basis of entirely reasonable "thermodynamic" solubility parameters, these numbers can be successfully explained.

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LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

The Crystal Structure of MnF_2, FeF_2, CoF_2, NiF_2 and ZnF_2

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The crystal structures of the five anhydrous fluorides have been checked by X-ray diffraction, using samples prepared from the melt, and precise lattice constants have been determined. All five fluorides have the rutile structure $D^{14}{}_{4h}$ − P4/mnm. The parameters, at 25°C., are: MnF_2, $a = 4.8734 \pm 0.0002$ Å., $c = 3.3099 \pm 0.0005$ Å., $u = 0.310 \pm 0.003$; FeF_2, $a = 4.6966 \pm 0.0002$ Å., $c = 3.3091 \pm 0.0001$ Å., $u = 0.305 \pm 0.01$; CoF_2, $a = 4.6951 \pm 0.0002$ Å., $c = 3.1796 \pm 0.0003$ Å., $u = 0.308 \pm 0.003$; NiF_2, $a = 4.6506 \pm 0.0002$ Å., $c = 3.0836 \pm 0.0004$ Å., $u = 0.310 \pm 0.003$; ZnF_2, $a = 4.7034 \pm 0.0002$ Å., $c = 3.1335 \pm 0.0003$ Å., $u = 0.307 \pm 0.003$.

In connection with a program of investigation of the magnetic and thermal properties of the anhydrous fluorides of divalent manganese, iron, cobalt, nickel and zinc, accurate values for the lattice constants of these compounds are needed. Data on MnF_2 have been reported previously.[1] Early work[2] on the structure of FeF_2, CoF_2, NiF_2 and ZnF_2 shows that these compounds all have the rutile structure, space group $D^{14}{}_{4h}$ − P4/mnm. Since the present work was begun Haendler, Patterson and Bernard[3] have reported precise lattice constants of NiF_2 and ZnF_2.

Preparation of Specimens.—One of the objects of this research was to obtain lattice constants of crystals of the metal fluorides which had been grown from the melt, as had the specimens used for our magnetic and thermal measurements. All previous crystal structure determinations of the iron-group fluorides have been upon powders prepared below the melting point and it is necessary to verify that the structure of material which has been melted is the same. For this reason we made measurements on NiF_2 and ZnF_2 to compare with the results of Haendler, Patterson and Bernard.[3] The ferrous fluoride and cobaltous fluoride samples were taken from boules which had supplied the single crystals used by Stout and Matarrese[4] for magnetic anisotropy measurements. Spectrochemical analysis showed 0.03% impurity in the FeF_2 and 0.02% in the CoF_2. The FeF_2 also contained 0.1% of ferric ion. Measurements also were made on some sublimed FeF_2 which had condensed in the crystal growing furnace. This material contained no detectable ferric ion and gave X-ray pictures identical with the other sample. Two samples of NiF_2 were used. One consisted of material which had been melted and the other was sintered material, taken from a sample used[5] in heat capacity measurements. Both samples gave identical X-ray patterns. Spectrochemical analysis of the sintered material, which was used for the back reflection photographs, showed 0.01% impurities. The ZnF_2 was from a melted sample used[5b] in heat capacity measurements. It contained 0.01% impurities. All samples were crushed in a mortar and material sieved through a 200-mesh cloth was used for the X-ray specimens.

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[1] M. Griffel and J. W. Stout, THIS JOURNAL, **72**, 4351 (1950).

[2] (a) V. M. Goldschmidt, "Geochem. Verteilungsgesetze," Vol. VI, Oslo, 1936 (measurements of W. Zachariasen); (b) A. Ferrari, *Atti accad. Lincei*, [6] **3**, 224 (1926).

[3] H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952).

[4] J. W. Stout and L. M. Matarrese, *Revs. Mod. Phys.*, **25**, 338 (1953).

[5] (a) J. W. Stout and E. Catalano, *Phys. Rev.*, **92**, 1575 (1953); (b) E. Catalano, Thesis, Univ. of Chicago, 1954.