and even compounds is also evident from a comparison of the distribution of diffraction intensity in reciprocal space, all members of the series showing regions of relatively high intensity in the same positions.

The effective cross-sections of the paraffin chains normal to their chain direction, calculated from $1/8a_0b_0 \cos \tau$, have an average value of 19.6 Å.^{2}, and show a slight decrease with increasing chain length.

The average molar volume increment is found to be 29.6 cm.^{3}/CH$_2$/mole.

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Densities and Thermal Expansion Coefficients of Several Organofluoro Compounds

BY GENE P. RUTLEDGE AND WILLIAM T. SMITH, JR.

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The densities of several liquid organofluoro compounds were determined (see Table I) in an attempt to find some liquid having an exceptionally high thermal expansion coefficient for an industrial application. The expansion coefficient, α, is defined as $(d_1 - d_2)/d_2(T_2 - T_1)$ where d_1 is the density at the lower temperature, T_1 and d_2 the density at T_2. Published density measurements[1] on perfluoro-*n*-heptane and perfluoro-1,3,5-trimethylcyclohexane indicate that large values of α might be expected for fluorine compounds.

TABLE I

DENSITIES AND THERMAL EXPANSION COEFFICIENTS OF ORGANOFLUORO COMPOUNDS AT VARIOUS TEMPERATURES

				Density, g./ml.					
Temp., °C.	Ethyl difluoroacetate	Ethyl trifluoroacetate	Benzotrifluoride	1,1,1-Trifluoro-2,3,3-trichloropropene	1,1-Difluoro-3,3-dichloropropene-2	*p*-Flurotoluene	*p*-Fluorobromobenzene	α-Fluoronaphthalene	α-Fluoroanisole
30.00	1.1600	1.1670	1.1762	1.5940	1.4401	0.9869	1.5859	1.1256	1.1054
40.00	1.1446	1.1466	1.1621	1.5753	1.4248	.9763	1.5710	1.1168	1.0948
50.00	1.1287	1.1260	1.1478	1.5549	1.4069				
60.00	1.1125		1.1353	1.5336	1.3881	.9548	1.5413	1.0995	1.0734
70.00	1.0958		1.1184	1.5117	1.3692				
80.00	1.0790		1.1033	1.4905	1.3503	.9329	1.5114	1.0821	1.0514
100.00						.9102	1.4803	1.0649	1.0297
120.00							1.4490	1.0464	1.0061
140.00							1.4167	1.0284	0.9824
160.00								1.0091	
Temp. range, °C.				Thermal expansion coefficient, α, $\times 10^5$					
30– 40	135	178	121	119	108	108	94	79	97
40– 50	141	183	124	131	127				
50– 60	145		129	139	135				
40– 60						113	96	78	100
60– 70	152		133	145	138				
70– 80	157		137	142	140				
60– 80						118	99	80	104
80–100						125	105	81	106
100–120							108	88	117
120–140							114	88	121
140–160								96	

All of the liquids used were purified by distillation. Calibrated, Sprengel type, Pyrex glass pycnometers having ground glass caps and an approximate capacity of 11 ml. were used. Agitation of the thermostatic fluid, 18 liters of mineral oil, was accomplished by two turbine pumps which brought the oil from the bottom of the lagged metal vessel to the surface. A De Khotinsky thermoregulator which activated a Fisher–Surfass electronic relay afforded temperature control of ±0.02°. The temperatures were measured using National Bureau of Standards thermometers. The average value of two density measurements was taken. From the precision of the temperature control, the accuracy of the weighing (±0.1 mg.) and the agreement obtained for duplicate samples, it is estimated that the coefficients are accurate to ±1% for a 10° range.

A comparison of the expansion coefficients of the fluorinated compounds (Table I) with values calculated from density measurements[2] on the corresponding unfluorinated compounds reveals, in general, that the coefficients are greater for the fluorinated compounds. For example, α-fluoroanisole has a coefficient 2% greater than anisole over the same temperature range. For α-fluoronaphthalene the coefficient is 3% greater than for naphthalene; *p*-fluorobromobenzene, 2% greater than bromobenzene and benzotrifluoride, 12% greater than toluene. Toluene and *p*-fluorotoluene have nearly identical coefficients.

Ethyl acetate has a high expansion coefficient, typical of esters. Ethyl difluoroacetate has an even higher coefficient and ethyl trifluoroacetate has a coefficient that is 31% greater than that of the

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[1] A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 375 (1947).

[2] "Annual Tables of Physical Constants," Sec. 301 (C), American Committee of Annual Tables, National Research Council, Princeton, New Jersey (1941).

difluoroacetate. In general, it appears that an increase in the extent of fluorination of an organic compound results in an increase in thermal expansion coefficient.

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Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. IV. Effect of Noble Gases

BY DAVID J. WILSON AND HAROLD S. JOHNSTON

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The rate of the reaction $N_2O_5 + NO \rightarrow 3NO_2$ has been shown by Smith and Daniels[1] and by Mills and Johnston[2] to be that of an elementary unimolecular reaction. At around 0.1 mm. pressure in a 22-liter flask, the reaction is homogeneous and definitely within the second-order region.[3] The low-concentration second-order rate constants of a series of gases have been reported.[4]

Using the 22-liter bulb, and the same method of interpreting the data as was used previously,[3,4] we have determined the low-concentration second-order rate constants of the noble gases and carbon tetrachloride. Reactant pressures were each about 0.08 mm., and foreign gas pressures ranged from 3 to 0.02 mm. Experimental results are given in Table I.

TABLE I

EXPERIMENTAL RESULTS

M gas	No. of points	Intercept, sec.$^{-1}$	Low concn. second-order rate constant, cc. mole^{-1} sec.$^{-1}$ × 10^5		Ratio to pure N_2O_5
			Value	Standard error	
He	27	0.0132	2.80	0.26	0.124
Ne	17	.0129	2.02	.32	.090
Kr	26	.0119	3.57	.23	.159
Xe	11	.0134	3.30	.95	.147
CCl_4	30	.0130	12.4	1.3	.551

As shown previously, the activating efficiency function of the state i above the critical energy, a_{Mi}, can be written as $a_{Mi} = b_{Mi}P_i$, that is, the relative activating efficiency is also the relative deactivating efficiency. The function b_{Mi} is further factored, $b_{Mi} = b_M f_{Mi}$, where b_M is the kinetic collision constant

$$b_M = N_0\left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \quad (1)$$

where N_0 is Avogadro's number; σ_1 and σ_2, the collision diameters of the colliding particles; M_1 and M_2, the molecular weights of the colliding particles; and R and T have their usual meaning. The function f_{Mi} is the efficiency factor for deactivation which in general may be a function of each state i and a different function for each foreign gas M.

If the collision constant can be calculated by 1, then the relative efficiencies with b_M factored out give the ratios $\overline{(f_M)}/\overline{(f_1)}$, where 1 stands for nitrogen pentoxide, and the bar indicates an average with respect to P_i over the excited states. If deactivation occurred at every collision or if f_{Mi} depended on the quantum states i of the reactant molecule only but not on the identity of the foreign gas M, this ratio would be unity every time. It is not. (See Table II. This table includes data calculated from reference 4.)

TABLE II

EFFICIENCY AND RELATIVE EFFICIENCY

M gas	Mol. wt.	Collision diameter, Å.	Low concn. rate const./kinetic collision const., $\overline{(f_M)} \times 10^{10}$	$\overline{(f_M)}/\overline{(f_1)}$
He	4	2.18[a]	6.02	0.0650
Ne	20	2.59[a]	7.95	.0855
A	40	3.64[a]	14.3	.154
Kr	83.8	4.16[a]	19.3	.208
Xe	131.3	4.85[a]	17.5	.189
N_2	28	3.75[a]	21.2	.228
NO	30	3.75	27.9	.300
CO_2	44	4.59[a]	35.9	.387
CCl_4	154	5.46	62.5	.673
SF_6	146	4.52	41.2	.443
N_2O_5	108	6.00	93.0	1.000

[a] From E. H. Kennard, "Kinetic Theory of Gases," McGraw–Hill Book Co., Inc., New York, N. Y., 1938, p. 149.

Furthermore, it is impossible to adjust the collision diameters of either nitrogen pentoxide or of the various M gases to obtain ratios $\overline{(f_M)}/\overline{(f_1)}$ that are equal to unity. For the molecular weights are accurately known, and the ratio, $(2\sigma_{N_2O_5}/\sigma_{N_2O_5} + \sigma_M)^2$, can never be greater than 4, which is not sufficiently large to account for the observed relative efficiencies of the noble gases and nitrogen. Thus, the efficiency function f_{Mi} does differ markedly from one gas to another. (These results do not answer the question as to whether or how the efficiency function varies over the states i of the reactant molecule.)

Relative efficiency increases slowly with molecular weight through at least krypton for the noble gases. It increases at constant molecular weight as one goes from noble gases to diatomic or polyatomic gases, and nitrogen pentoxide is much more efficient than anything else we have yet used. A study of the relative efficiencies of diatomic and polar gases is now in progress.

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[1] J. H. Smith and F. Daniels, THIS JOURNAL, **69**, 1735 (1947).

[2] R. L. Mills and H. S. Johnston, *ibid.*, **73**, 938 (1951).

[3] H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951).

[4] H. S. Johnston, *ibid.*, **75**, 1567 (1953).