

Perhaps carbonium ions are also produced as intermediate substances; however, their existence is not required to explain any of the observations. One can account for the formation of completely fluorinated substances by considering these steps to be repeated until all hydrogen atoms have been removed and any resulting double bonds saturated.

As fluorination progresses, the bond-strengthening influence of $-CF_2-$ groups makes the substitution of the last few hydrogen atoms more difficult; therefore, the reaction temperature must be increased.

Step five accounts for the presence of a trace of

perfluorocyclopentane in the products resulting from the fluorination of *n*-pentane. Successive steps of ring closure followed by ring opening could lead to isomerization as the fluorination of the hydrocarbon proceeds. The purity of the products obtained indicates that such an isomerization is not extensive in the cases of normal and isopentane. The isomerization which occurs during the fluorination of neopentane is probably of a different type.

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Physical Properties of Perfluoropentanes^{1a}

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Melting points, transition temperatures, densities and viscosities of carefully purified perfluoro-*n*-pentane, perfluoroisopentane and perfluorocyclopentane, have been determined. In many ways perfluoro-*n*-pentane is very much like its isomer perfluoroisopentane. Their properties differ somewhat, however, in directions opposite to those found for the corresponding hydrocarbons. The theoretical significance of the results is discussed.

The wide interest in the physical properties of the fluorocarbons in recent years has centered to a large extent about the low intermolecular forces which are operative in these molecules. The weakness of these forces must be due to a large extent to the shell of tightly bound fluorine atoms. Simons² first called attention to the high volatility of these compounds and noted the regular increase of boiling point with molecular weight. The fluorocarbon data summarized by Grosse and Cady³ in 1947 confirmed this, and these authors showed that this regular progression with molecular weight held for many other physical properties. It was found, for example, that the viscosity of a fluorocarbon lubricant could be predicted from a knowledge of only its boiling range.

Nevertheless, it was felt that a more detailed study of the simple fluorocarbons might reveal significant differences in properties as structure and symmetry were changed. There seemed to be no good reason to conclude that this influence of structure should be parallel to that known to exist for the hydrocarbons. To investigate the effect of molecular configuration on the properties of the liquid and solid state, pure samples of the fluorocarbon pentanes were prepared.⁴ Their boiling points were determined and the viscosities and densities were measured over a wide temperature range. The vapor pressures and energies of vaporization were determined by Barber in connection with other research and are the subject of another paper.⁵ The pentanes were chosen because of their relative simplicity of structure, convenient liquid range and the availability of all of the pure hydrocarbons as starting materials.

Experimental

To avoid volatilization and to prevent condensation of water at the lower temperatures, all measurements were made in closed systems and transfers from storage vessels to the measuring apparatus were made by distillation. Stopcocks and ground joints were lubricated with "Apiezon L." Because of its extremely low volatility, this grease could not appreciably contaminate the fluorocarbons. As an added precaution, the liquids were not permitted to come in contact with the lubricated parts.

Melting points were determined from warming and cooling curves, using apparatus patterned after that of Skau⁶ and described by Sturtevant.⁷ A 2-g. sample of the substance to be studied was placed in a bulb equipped with a thermocouple held in a well. Surrounding the bulb was a cylindrical shell of copper, to which a second thermocouple was attached. This assembly was held in a double walled glass vessel surrounded by a bath of liquid at a known temperature. During a run the rate of temperature change of the metal shell was held at approximately 0.1° per minute by controlling the temperature of the bath and by regulating the pressure of air between the walls of the glass vessel. Temperatures of the shell and the sample were recorded alternately once a minute. From the area between the time-temperature curve of the sample and that of the outer shell an estimate of the heats involved in the various transitions and fusions was made. For this purpose the apparatus was calibrated with the hydrocarbons, *n*-pentane and isopentane, and also with mercury. The ΔH and C_p values used for the pentanes were those of Parks, Huffman and Thomas.^{8,9} Data regarding mercury were taken from the International Critical Tables.

Densities were determined with two Pyrex pycnometers each consisting of a bulb to which was sealed a calibrated section of capillary tubing. Above this capillary was a small expansion bulb and finally a micro-stopcock. As a test of the apparatus the density at 25° of fractionally distilled carbon tetrachloride was measured and found to be 1.5844 g./cc., a value which compares well with 1.58426 and 1.58414 of Scatchard¹⁰ and 1.5845 given by Timmermans and Martin.¹¹ Densities of the fluorocarbons were measured with

(1) (a) Presented at Meeting of the American Chemical Society, Portland, Oregon, Sept., 1948; (b) Senior author.

(2) J. H. Simons and L. Block, *THIS JOURNAL*, **61**, 2962 (1939).

(3) A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

(4) E. J. Barber, L. L. Burger and G. H. Cady, *THIS JOURNAL*, **73**, 4241 (1951).

(5) E. J. Barber, Thesis, University of Washington, 1948.

(6) E. L. Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1932).

(7) J. M. Sturtevant, Chapter X, in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945.

(8) G. S. Parks, *et al.*, *THIS JOURNAL*, **52**, 1032 (1930).

(9) G. S. Parks and H. M. Huffman, *ibid.*, **52**, 4381 (1930).

(10) G. Scatchard, *et al.*, *ibid.*, **61**, 3206 (1939); **62**, 712 (1940).

(11) J. Timmermans and F. Martin, *J. Chim. Phys.*, **23**, 747 (1936).

TABLE I
 MELTING AND TRANSITION TEMPERATURES

Compound	Lower transition, °K.	ΔS lower trans., e.u.	Higher transition, °K.	ΔS higher trans., e.u.	Melting point, °K.	ΔS melting, e.u.
<i>n</i> -C ₅ F ₁₂	"		144.6 ± 0.5	"	147.8 ± 0.4	11
Iso-C ₅ F ₁₂	"		"		176.5 ± .5	2
Cyclo-C ₅ F ₁₀	115.5 ± 0.3	"	118.2 ± 0.3	10	283.5 ± .1	3
<i>n</i> -C ₅ H ₁₂	"		"		143.4	14.0
Iso-C ₅ H ₁₂	"		"		112.6	10.9
Cyclo-C ₅ H ₁₀	121.6	11.01	137.1	0.624	179.0	0.807

^a Transition not observed at temperatures above 90°K. ^b Included in ΔS for higher transition. ^c Included in ΔS for melting.

the liquids held under their own vapor pressures. From a rough value of the compressibility determined for perfluoro-*n*-pentane, 33×10^{-6} atm.⁻¹ at 25°, it was computed that these densities would differ from those at 1 atm. by less than 0.0002 g. cm.⁻³. Tests indicated that the pycnometer could be carried through the procedures of pumping, filling, immersion in a thermostat containing water or acetone, emptying, etc., with a variation of less than 0.2 mg. Corrections were made for the weight of fluorocarbon vapor, buoyancy of air and expansion of the glass. The densities are considered accurate to ± 0.0005 unit at the higher and ± 0.001 at the lower temperatures.

Viscosities were measured in two Ubbelohde¹² suspended level viscometers. The capillaries for the viscometers had radii of 0.141 mm. and 0.215 mm. with variations in diameter of less than 1%. Times of flow for the 5-ml. volume varied from 170 to 1700 seconds. The viscometers were fitted at the top with micro-stopcocks, and nitrogen gas was used to force the liquid to the upper bulb preparatory to making a measurement. When connections to the N₂ line or to the atmosphere were required, traps cooled by liquid air prevented moisture from entering the system.

Distilled water was used as the calibrating liquid and the calibration was performed at four temperatures, using the data of Bingham and Jackson¹³ as a standard.

The constants *A* and *B* for the equation, $\eta/\rho = At + B/t$, where ρ is the density and *t* is the time in seconds, were calculated. The constants were also computed¹⁴ from the dimensions of each viscometer and were found to agree reasonably well with the calibration.

The viscosity of purified carbon tetrachloride at 25° was determined to be 9.157 millipoises. Literature values vary over a 7% range with a mean close to the above figure.

The high temperature coefficients of expansion and viscosity necessitated careful temperature control. Water was used for the bath at temperatures above 0° and acetone below 0°. Temperature variation at the higher temperatures was less than 0.02°, but at Dry Ice temperatures and below, control to better than $\pm 0.1^\circ$ was not always achieved.

The viscosity measurements were reproducible to 0.3%, above 0° to about 0.6% at -50° and 1%, below Dry Ice temperatures.

Results and Discussion

Melting Point.—Data regarding melting and transitions for the perfluoropentanes and for the corresponding hydrocarbons are summarized in Table I. Values given for the hydrocarbons are those of Parks and his associates.^{8,9,15} Since entropy changes for the fluorocarbons were estimated only from warming curves, the values given may be in error by as much as 30%.

Attention is called to the following similarities and differences shown in the table: (1) The two cyclo compounds are much alike in their melting and transition properties. Their high melting points

are in accord with the symmetrical structures of the molecules. (2) The normal and isofluorocarbons differ much from the hydrocarbons. The entropies of fusion of the fluorocarbons are low and the melting point of the iso compound is higher than that of the normal.⁸ Low entropies of fusion for all of the fluorocarbons suggest the possibility that molecules in the solids may rotate at temperatures above the upper transition points.

Recently Simons and Dunlap¹⁶ have described several of the physical properties of perfluoro-*n*-pentane. Their values for the melting and transition points (147.51 and 144.51°K.) agree well with those given in Table I.

It has been reported in the literature that many of the fluorocarbons solidify to glasses when cooled. In outward appearance, the compounds, studied in this research are glass-like in the solid state. If cooled slowly past the melting point, the solid which forms appears to lack the plane surfaces characteristic of a crystal. The mass has curved surfaces and looks like glass. The sharpness of the melting point and the high fluidity of the liquid at its melting point suggest, however, that the solids are crystalline. The crystalline structure of a similar fluorocarbon, perfluorocyclohexane, was established by Christoffers, Lingafelter and Cady by X-ray diffraction.¹⁷ It is probable, therefore, that fluorocarbon "glasses," except for oils of extremely high viscosity, are actually transparent crystals.

Density.—The three fluorocarbons differ appreciably in density as one may see by comparing the data in Table II. Values enclosed in parentheses in this table have been estimated from the others. Table III permits one to compare the fluorocarbons with the corresponding hydrocarbons both at 20° and at the boiling points of the compounds. Data for the hydrocarbons are taken from the literature. Perfluoroisopentane is more dense and less volatile than the normal compound, a difference opposite to that for the hydrocarbons.

The high coefficients of expansion of the fluorocarbons are of interest. This coefficient is highly dependent upon temperature as shown by the fact that for perfluoro-*n*-pentane it increases from 0.0014 deg.⁻¹ at -85° to 0.0021 deg.⁻¹ at 30°. Over the range from freezing point to boiling point this compound increases in volume 42 cc. mole⁻¹ or about 30%.

Simons and Dunlap¹⁶ have published an equation representing the relationship between temper-

(12) L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, **9**, 85 (1937).

(13) E. C. Bingham and R. F. Jackson, *Bull. Bur. Stds.*, **14**, 59 (1918).

(14) G. Barr, "A Monograph of Viscometry," Oxford University Press, London, 1931.

(15) C. S. Jacobs and G. S. Parks, *THIS JOURNAL*, **56**, 1513 (1934).

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

(17) H. J. Christoffers, *et al.*, *THIS JOURNAL*, **69**, 2502 (1947).

TABLE II
 DENSITIES OF PERFLUOROPENTANES

$n\text{-C}_5\text{F}_{12}$		iso- C_5F_{12}		cyclo- C_5F_{10}	
Temp., °C.	Density, g./cc.	Temp., °C.	Density, g./cc.	Temp., °C.	Density, g./cc.
29.98	1.5869	30.80	1.6286	22.51	1.6370
28.14	1.5932	29.86	1.6317	21.96	1.6388
26.30	1.5995	23.99	1.6514	21.17	1.6413
(20.00)	(1.6200)	20.03	1.6645	20.55	1.6436
19.20	1.6223	(20.00)	(1.6645)	(20.00)	(1.6451)
17.73	1.6276	17.55	1.6726	18.92	1.6486
15.25	1.6351	17.33	1.6739	18.78	1.6490
14.67	1.6372	15.45	1.6793	18.68	1.6495
12.67	1.6437	14.39	1.6833	17.73	1.6523
10.65	1.6502	13.40	1.6859	16.70	1.6556
1.30	1.6800	10.22	1.6967	15.80	1.6583
0.30	1.6830	9.21	1.7000	15.80	1.6586
(0.00)	(1.6838)	2.17	1.7221	14.62	1.6622
-9.35	1.7128	(0.00)	(1.7287)	14.36	1.6630
-17.13	1.7359	-13.14	1.7691	13.71	1.6652
-31.30	1.7772	-17.06	1.7808	13.70	1.6649
-65.19	1.8727	-39.14	1.8455	12.23	1.6697
-74.06	1.8971	-52.19	1.8832	11.56	1.6715
-88.19	1.9356	-67.65	1.9267	11.17	1.6731
		-78.98	1.9579	10.75	1.6744
		-88.91	1.9851	10.56	1.6749

ature and the density of perfluoro-*n*-pentane over a temperature range from 258 to 283°K. Within these temperature limits the equation is in good agreement with the data in Table II. It is not satisfactory, however, at temperatures much below 258°K.

TABLE III

Substance	Density at 20°, g./cc.	Boiling point, °C.	Density at b.p., g./cc.	Molar volume at 20°	Molar volume at b.p.	Coef. of expansion at 15°
$n\text{-C}_5\text{F}_{12}$	1.620	29.3	1.585	178	182	0.00197
Iso- C_5F_{12}	1.664	30.1	1.631	173	177	.00193
Cyclo- C_5F_{10}	1.645	22.5	1.637	152	153	.00193
$n\text{-C}_5\text{H}_{12}$	0.626	36.1	0.611	115	118	.00153
Iso- C_5H_{12}	0.620	28.0	.613	116	118	.00155
Cyclo- C_5H_{10}	0.746	49.5	.715	94	98	.00126

The density of solid perfluorocyclopentane at 9.5° was found by adjusting the composition of an aqueous solution of ZnCl_2 until it just suspended a crystal of the fluorocarbon. A value of 1.84 was obtained. The liquid density at the melting point is 1.676, corresponding to a volume change on fusion of 13.3 cc./mole. This amount together with the heat of fusion gives as the effect of pressure on the melting point, the very high value, 0.1°/atm.

Viscosity.—Viscosities of the pure fluorocarbons are listed in Table IV. In Table V the viscosities at 20° of the fluorocarbons and hydrocarbons are compared. As in the case of the densities at this temperature, the normal and isofluorocarbons differ from each other in a direction opposite to that found for the corresponding hydrocarbons.

If the viscosities of the pentane hydrocarbons are compared at corresponding temperatures, that of the straight chain isomer is found to be lower. A comparison of fluorocarbons with hydrocarbons on the basis of viscosity at the boiling point reveals a trend in viscosity in the order cyclo > iso > normal in both series. However, the relative differences in the two families are not the same. The perfluoro-*n*-pentane and perfluoroisopentane, for example, have a greater difference than do the corresponding hydrocarbons. These data point to the

 TABLE IV
 VISCOSITIES OF PERFLUOROPENTANES

$n\text{-C}_5\text{F}_{12}$		iso- C_5F_{12}		cyclo- C_5F_{10}	
Temp., °C.	η , milli- poises	Temp., °C.	η , milli- poises	Temp., °C.	η , milli- poises
24.90	4.619	21.60	6.107	21.55	7.489
23.53	4.708	20.93	6.178	20.05	7.670
15.28	5.273	13.66	6.954	15.84	8.274
14.11	5.349	3.78	8.238	12.56	8.758
6.28	5.996	-9.16	10.47	12.05	8.857
2.45	6.342	-19.45	12.93	10.36	9.139
-4.74	7.087	-34.96	18.44		
-18.32	8.856	-46.71	25.11		
-35.95	12.31	-54.21	31.38		
-36.61	12.45	-59.09	36.42		
-51.45	16.91	-62.90	41.57		
-58.18	19.85	-71.28	55.80		
-63.37	22.66	-74.93	64.39		
-67.62	25.65	-79.4	77.49		
-76.10	32.61				
-79.17	35.98				
-84.61	43.15				
-88.41	49.61				

TABLE V

COMPARISON OF VISCOSITIES OF PENTANES¹⁸

Compound	η_{20}	$\eta_{b.p.}$
$n\text{-C}_5\text{F}_{12}$	4.94	4.38
Iso- C_5F_{12}	6.28	5.36
Cyclo- C_5F_{10}	7.67	7.27
$n\text{-C}_5\text{H}_{12}$	2.32	2.01
Iso- C_5H_{12}	2.23	2.08
Cyclo- C_5H_{10}	4.37	3.25

importance of molecular shape in determining the viscosity of a fluorocarbon.

Theoretical treatments of the viscosity of liquids lead to an equation of the form $\eta = Ae^{B/T}$ in which A and B are constants and T is the absolute temperature. This relationship describes well the behavior of the perfluoropentanes at viscosities up to about 30 millipoises. At higher values, however, the observed viscosities become increasingly greater than those calculated from the equation.

Eyring¹⁹ in his theoretical discussion of liquid flow has shown that the ratio $\Delta E_v/E_{vis}$, (molar energy of vaporization)/energy of activation for flow), has values close to 4 and 3, respectively, for nearly all unsymmetrical and symmetrical molecules. He also has found that the ratio $\Delta E_v/\Delta F^\ddagger$, in which ΔF^\ddagger is the free energy of activation for flow has values close to 2.45 for a large number of substances. His theory predicts that the viscosities of perfluorocyclopentane and perfluoroisopentane at their melting points should be 3.5 and 7.0 millipoises, respectively. The unusual behavior of fluorocarbons is illustrated by the fact that the two substances just mentioned have viscosities at their melting points of 9.15 and 180 millipoises and that energy ratios for the three perfluoropentanes have the low values

(18) Hydrocarbon data are from the "International Critical Tables," Landolt-Bornstein, and Doss "Physical Properties of Principal Hydrocarbons," Texas Co., New York, N. Y., 1939. Considerable variation is found in the literature for the viscosities of the hydrocarbons especially for cyclopentane.

(19) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," Chapter 9, McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

given in Table VI. In this table ΔS^\ddagger is the entropy of activation for flow. The low values for the ratio $\Delta E_v/E_{vis}$ may be interpreted to mean the size of a "hole" required to permit movement of a molecule to a new equilibrium position is a larger fraction of the actual volume of a molecule than is needed for most other compounds including hydrocarbons. Fluorocarbon molecules, therefore, appear to be either more closely packed or less flexible than hydrocarbon molecules.

TABLE VI

COMPARISON OF ENERGY TERMS FROM VISCOSITY DATA							
Compound	t , °C.	E_{vis} , kcal. mole ⁻¹	ΔF^\ddagger , kcal. mole ⁻¹	ΔS^\ddagger , e. u.	ΔE_v , kcal. mole ⁻¹	$\Delta E_v/\Delta F^\ddagger$	$\Delta E_v/E_{vis}$
<i>n</i> -C ₅ F ₁₂	-80	2.42	2.78	-2.4	7.62	2.7	3.1
	-50	2.24	2.87	-3.6	7.14	2.5	3.2
	20	2.24	3.14	-4.0	6.05	1.9	2.7
Iso-C ₅ F ₁₂	-80	3.23	3.06	-0.4	7.96	2.6	2.5
	-50	2.89	3.09	-1.7	7.16	2.3	2.5
	20	2.69	3.26	-2.7	6.05	1.9	2.2
Cyclo-C ₅ F ₁₀	10	2.94	3.28	-2.4	5.91	1.8	2.0
	20	2.94	3.30	-2.4	5.76	1.7	2.0

The latter alternative is the more reasonable. The other ratio $\Delta E_v/\Delta F^\ddagger$ is not found to be constant nor is it equal to 2.45 as found by Eyring for a large number of compounds. It is apparent that the ratio obtained is highly dependent upon the temperature.

Constancy of the ratio $\Delta E_v/E_{vis}$ is expected if the activation energy $E_{vis} \cong \Delta H^\ddagger$, arises almost entirely from the energy of hole formation. Bondi²⁰ in an attempt to analyze the energy terms suggests that ΔE_v be compared with the actual energy of hole formation $\Delta H^{\ddagger h}$. The other part of ΔH^\ddagger , $\Delta H^{\ddagger j}$, is the energy required to transport the molecule to the new equilibrium position. It includes rotational barriers. If one assumes that $\Delta E_v/\Delta H^{\ddagger h}$ is constant, then $\Delta H^{\ddagger j}$ for the perfluoropentanes increases rapidly in the order *n*-, iso-, cyclo-. It is quite possible that $\Delta H^{\ddagger j}$ comprises a larger fraction of the activation energy in the case of fluorocarbons than for most other types of compounds.

Values for ΔS^\ddagger indicate that the degree of orientation required for activation at room temperature is greatest for perfluoro-*n*-pentane and least for perfluorocyclopentane.

It is seen that the viscosity functions indicate clearly differences between the three compounds. It was of interest, therefore, to study a mixture of the fluorocarbons. Table VII lists data for a mixture of perfluorocyclopentane and perfluoro-*n*-pentane in which the mole fraction of the former is 0.544. Subscripts 1, 2 and m refer, respectively, to cyclo-, to *n*- and to the mixture.

The mixture densities, ρ_m , in the table were obtained by extrapolation of measurements made at

(20) A. Bondi, *J. Chem. Phys.*, **14**, 591 (1946).

TABLE VII

THE VISCOSITY OF A MIXTURE OF PERFLURO-*n*-PENTANE WITH PERFLUROCYCLOPENTANE

Temperature, °C.	η_1 , millipoises	η_2 , millipoises	η_m , millipoises	ρ_m , g./cc.
5.0	10.14 ^a	6.090	7.743	1.6804
15.0	8.395	5.282	6.573	1.6488

^a Calculated by extrapolation of data taken above melting point, 10.30.

15 and 12°. The densities calculated from the assumption that the volumes are additive agreed within 0.02%.

From the equation of Eyring,¹⁸ $\eta = hN/Ve^{\Delta F^\ddagger/RT}$, the viscosity of a mixture which approaches ideality can be expressed in the form

$$\ln \eta_m = \sum N_i \ln \eta_i V_i/V_m + (\Delta F_m^\ddagger - \sum N_i \Delta F_i^\ddagger)/RT$$

where N_i is the mole fraction of the *i*th component and V_i its molar volume. The subscript m denotes the mixture. Since these are measurable quantities, the differences between the "ideal" free energy of activation, $\sum N_i \Delta F_i^\ddagger$, and the observed ΔF_m^\ddagger can be computed from the equation. The quantity $\sum N_i \Delta F_i^\ddagger - \Delta F_m^\ddagger$ at 5° and 15° was found to be 18 ± 7 cal./mole and 17 ± 7 cal./mole, respectively. This difference should be of the same order of magnitude as the excess free energy of mixing. Thus, while only a small abnormality is indicated, one might expect to find a small excess free energy of mixing of perfluorocyclopentane with perfluoro-*n*-pentane.

Compressibility.—The high value of the temperature coefficient of expansion, α , of the liquid fluorocarbon has already been mentioned. Perfluoro-*n*-pentane shows the highest expansion, 0.00206 deg.⁻¹ at 25°. An approximate value for the compressibility, β , at 25° was obtained for this compound with the aid of the pycnometer described above, and was found to be 33×10^{-5} atm.⁻¹. From these coefficients one may calculate the "internal pressure," $T\alpha/\beta$ to be 1790 atmospheres. This value differs considerably from 1380 atmospheres, the internal pressure, corresponding to the energy of vaporization per cc. of liquid. It is common for the two methods of calculation to give different values for internal pressures, but the difference is usually less than in the case of this fluorocarbon. For example, $T\alpha/\beta$ for the hydrocarbon *n*-pentane is 1920 atmospheres at 25° while the energy of vaporization per cc. corresponds to 2020 atmospheres.

One may judge from the physical constants given in this paper that the two isomeric pentanes are more nearly alike than their hydrocarbon analogs but that they do differ appreciably. The differences in general are opposite to those for the hydrocarbons.

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