U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP915

Part of Journal of Research of the National Bureau of Standards, Volume 17, September 1936

EMPIRICAL RELATION BETWEEN THE ATOMIC DIMENSIONS AND THE MELTING AND SUBLIMATION POINTS OF THE NOBLE GASES, HALOGENS, AND ELEMENTS OF THE SULPHUR GROUP

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ABSTRACT

In comparing the melting points of the noble gases, halogens, and elements of the sulphur group the author found that those elements of these groups which have analogous differences in atomic structure show an apparent relationship between their melting points and their atomic dimensions, the differences in the melting points being proportional to the differences between the corresponding atomic radii. Further, it was found that for these elements with analogous differences in atomic structure an apparent proportionality exists between the differences in the atomic radii and the differences in the sublimation points at low pressure.

CONTENTS

I. INTRODUCTION

A relationship between optical rotation and atomic dimension has been previously pointed out and is being studied by the writer.[1] Other relations such as chemical affinity in which atomic dimensions seem to play a role were also observed.[2] Since halogen *derivatives* were used for the investigation of these relations it seemed desirable to look for any apparent relationship between the physical characteristics of the halogen *elements* and their atomic dimensions and to extend the study to other available groups of elements. The present paper embodies the results of this study.

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[1] BS J. Research **7,** 573 (1931) RP358; J. Am. Chem. Soc. **56,** 1421 (1934).
[2] J. Am. Chem. Soc. **45,** 2385 (1923).

II. RELATIONSHIP BETWEEN ATOMIC RADII AND MELTING POINTS FOR ELEMENTS WITH ANALOGOUS DIFFERENCES IN ATOMIC STRUCTURE

In studying the relationship between atomic radii and melting points, comparisons have been made, using the noble gases, halogens, and elements of the sulphur group. Hydrogen has been included in the group of the halogens as it often behaves in a manner analogous to that of the halogens both as free elements and in organic compounds.[3] The data are given in table 1.

It will be observed from table 1:

(1) That for the heavier elements of the noble gases, of the halogens, and of the sulphur group (A, Kr, Xe), (Cl, Br, I), and (S, Se, Te) the ratio $\frac{\Delta \mathrm{ar}}{\Delta \mathrm{mp}} \times 10^{-2}$ agrees well since (A, Kr, Xe) show 0.46 and 0.46; further (Cl, Br, I) show 0.14 and 0.15; and finally (S, Se, Te) 0.11 and 0.10.

(2) Also that the lighter elements of the noble gases (He, Ne, A) show an agreement 0.78 and 0.71, and the lighter elements of the halogen group (H, F, Cl) show 0.33 and 0.34. However, the ratio for (He, Ne, A), 0.71, differs from the ratio for the heavier elements (A, Kr, Xe), 0.46. This ratio is still smaller for the lighter halogens (H, F, Cl), 0.33, decreasing further for the heavier halogens, 0.14, and still further for the sulphur elements to 0.11. The less accurate agreement for (He, Ne, A) may be due to the nonsolidification of He under its own vapor pressure. The above relationship in the cases where it is found to hold can be correlated to and explained by the structure of the atoms. Comparing the structure of atoms built up in successive electron shells,[4] the writer observed that the noble gases (which will serve as the basis for all comparisons) can be arranged into two groups, as shown in table 2.

	Melting Points	Atomic Radii in A ^{a}	Ratio $\frac{\Delta ar}{\Delta mp} \times 10^{-2}$
	Noble gases		
He	(-273.1)	0.93	
Ne	-248.7	1.12	(0.78)
A	-189.3	1.54	.71
Kr	-157	1.69	.46
Xe	-112	1.90	.46
	Halogens		
H	-259.1	0.53	
F	-217	0.67	.33
Cl	-102.5	1.05-1.07	.34
Br	- 7.3	1.19	.14
I	114.1	1.36-1.40	.15
	Elements of the sulphur group		
O	-218.4	0.60	
S	112.8	1.02-1.04	.13
Se	220.2	1.13-1.17	.11
Te	453	1.33-1.43	.10

(References to the data used are given at the end of this article, pages 343–345)

TABLE 1.—*Comparison of melting-point differences of the noble gases, halogens, and elements of the sulphur group with atomic-radii differences*

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[3] Van Arkel and De Boer, Z. Physik **41,** 27 (1927).

[4] Kramers and Holst, De Bouw der Atomen (Amsterdam, ed. 2, p. 169, 1930).

Group (He, Ne, A).—Ne differs from He, and A from Ne in an identical manner by the presence of 8 electrons in groups of 2 and 6 in the next energy level.

Group (A, Kr, Xe).—Kr differs from A, and Xe from Kr in an identical manner by the presence of an energy level of 18 electrons in groups of 2, 6, and 10 inserted below the outer energy level.

Energy level or main quantum number	K	L		M			N				O	
	1 Quantum	2 Quanta		3 Quanta			4 Quanta				5 Quanta	
Noble Gases												
He	2											
Ne	2	2	6									
A	2	2	6	2	6							
A	2	2	6	2	6							
Kr	2	2	6	2	6	10	2	6				
Xe	2	2	6	2	6	10	2	6	10		2	6
Halogens												
H	1											
F	2	2	5									
Cl	2	2	6	2	5							
Cl	2	2	6	2	5							
Br	2	2	6	2	6	10	2	5				
I	2	2	6	2	6	10	2	6	10		2	5
Elements of the Sulphur Group												
O	2	2	4									
S	2	2	6	2	4							
S	2	2	6	2	4							
Se	2	2	6	2	6	10	2	4				
Te	2	2	6	2	6	10	2	6	10		2	4

TABLE 2.—*Groupings of electrons in the atoms.*

By omitting one outer electron, group (He, Ne, A) yields group (H, F, Cl) and by omitting one and two outer electrons, respectively, group (A, Kr, Xe) yields the groups (Cl, Br, I) and (S, Se, Te), respectively, which show the same melting-point relation.

The group of the alkali and earth alkali metals do not show any regularities, which is probably connected with the exceptional elliptical comet orbit of their outer electrons. Evidence is thus obtained that the noble gases, halogens, and elements of the sulphur group can be divided into two groups based on analogous difference in electronic structure, which is paralleled by an identical division based on the ratio of the successive differences in atomic radii to the respective differences in melting points $\left(\frac{\Delta \mathrm{ar}}{\Delta \mathrm{mp}}\times 10^{-2}\right)$.

III. RELATIONSHIP BETWEEN ATOMIC RADII AND SUBLIMATION POINTS AT LOW PRESSURE FOR THE SAME ELEMENTS

It may be expected from the above discussed melting-point–atomic-dimension relation and the well known rule of Ramsay and Young that atomic-dimension differences may be related in the same simple way to temperature differences for the above sets of elements for any definite pressure at which two phases are in equilibrium.

This rule of Ramsay and Young [5] states that for closely related substances the ratio of the absolute temperatures corresponding to equal vapor pressures of the liquid is constant. The authors derived this rule from the vapor pressures of ethyl chloride, ethyl bromide, and ethyl iodide, and also for chloro and bromo benzene for which vapor pressure data for the liquid phases were available. By a simple mathematical deduction the rule of Ramsay and Young may also be stated as follows: The ratio of phase-equilibrium temperature differences for a group of closely related substances is constant at all pressures. However, by making a graphical comparison of p–t relations for the above mentioned groups of elements, (He, Ne, A), (A, Kr, Xe), (Cl, Br, I), etc. (using for each group the same axes of coordinates by which temperature differences for a certain pressure can be easily read on lines parallel to the X axis) two observations were made which cannot be derived by the above considerations:

(Br-Cl):(I-Br)

Pressure in mm Hg	Ratio of phase-equilibrium temperature differences	Ratio of atomic-dimension differences
Solid phases		
0.0025	17.1 : 22.0	17.1 : 21.8 (from melting-point relation)
0.0090	17.1 : 22.3	
0.030	17.1 : 22.2	17.1 : 21.4 (from optical-rotation relation)
0.25	17.1 : 23.2	
8	17.1 : 22.6	
Different phases		
20	17.1 : 23.2	
60	17.1 : 23.3	
80	17.1 : 23.2	
Liquid phases		
110	17.1 : 23.3	
180	17.1 : 23.0	
370	17.1 : 23.3	
465	17.1 : 23.2	

TABLE 3.

(1) The ratio of phase-equilibrium temperature differences for these groups of elements is not quite constant but tends to approach a value equal to the ratio of the respective atomic-dimension differences only at the lowest pressures.

(2) In this graphical comparison the melting points for a group of elements are situated on a straight line.

The most reliable data for checking the first observation are those for the (Cl, Br, I) group.[6] The data are given in table 3.

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[5] Phil. Mag. **20**, 530 (1885); also **21**, 33 (1886).

[6] Also for the group (A, Kr, Xe) it was found that the ratio of the temperature differences (Kr–A): (Xe–Kr at the lowest pressure measured (22 mm) is 15:21.2, agreeing very well with the atomic-dimension differences (15:21), and further that the deviation becomes more pronounced the higher the pressure. That this deviation for higher pressures for the group (A, Kr, Xe) is in the opposite direction to the deviation for (He, Ne, A) and also for the group (Cl, Br, I) could not be explained (see also footnote 8). The temperature relationship for the group (He, Ne, A) does not show a close agreement at the lowest pressure measured. This ratio is 19:49.9 at 22 mm, whereas the ratio for the atomic-dimension differences is 19:42. It is obvious that in this relationship as in the melting-point relation the behavior of He is not strictly comparable with that of Ne and A. However, for 25.8 kg/cm² the melting point relation for these elements is 19:46.5; for 145.3 kg, 19:50.5; and for 1,800 kg, 19:59, showing the tendency to diminish to the atomic-dimension ratio at ordinary pressure.

The ratio for the atomic-dimension differences (Br–Cl):(I–Br), 17.1:21.4, was obtained by the author from the investigation of optical rotation and atomic dimension. A discussion of the available data, including the Goldschmidt values was also given.[7,8] It will be seen that this ratio agrees very closely with that calculated from the melting-point relation (table 1) and also with that for the phase-equilibrium temperature relation for the lowest pressure determined (0.0025 mm, table 3). Above 0.25-mm pressure the ratio deviates appreciably.

From the second observation that the melting points of Cl, Br, and I are situated on a straight line in the graphical comparison a deduction can be made. If a line be drawn through the melting point of chlorine parallel to the X axis, and lines perpendicular thereto through the melting points of bromine and iodine, similar triangles are formed thereby. If the melting-point-atomic dimension ratio holds for these elements, as suggested above, it follows that the distance between the melting points on the straight line will have the same ratio as the respective atomic-dimension differences. The same peculiarity may hold for (S, Se, Te), although experimental data are conflicting and are complicated by the presence of allotropic forms. The data of different investigators for the vapor pressures at the melting points for Kr and Xe disagree to such an extent[9] that the group (A, Kr, Xe) cannot be tested for this peculiarity (see fig. 1). Its existence cannot be determined for (He, Ne, A) as He probably cannot be obtained in the solid phase under its own vapor pressure. In figure 3 an application of this observation was made, indicating that ordinary hydrogen belongs in the series with F and Cl and not deuterium. However, the melting point of F has not been recorded with sufficient accuracy for checking the regularity.

IV. CONCLUSIONS

From the discussion given above it is clear that there is evidence that existing data indicate relationships between melting points, and also phase-equilibrium temperatures at low pressure, and atomic dimensions for elements with analogous differences in atomic structure.

The relationships indicated are especially interesting owing to the fact that melting points and phase-equilibrium temperatures at low pressures are not directly atomic properties but are properly included in the phase theory.

The author expresses his thanks to Frederick Bates for his interest and suggestions.

V. PRESSURE-TEMPERATURE CURVES

(Figures 1, 2, and 3)

Note.—The values used for calculating the ratios (Ne–He): (A–Ne); (Kr–A): (Xe–Kr); (Br–Cl): (I–Br); and (F–H): (Cl–F) were obtained from the original accurately constructed large-scale figures plotted on millimeter cross-section paper, of which figures 1 and 2 are reproductions.

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[7] See footnote 1, p. 337.

[8] J. Am. Chem. Soc. **47**, 1280 (1925). In this connection it is noteworthy that the relationship between optical rotation and atomic dimension holds not only for Cl, Br, and I derivatives but also includes the F and most probably also the H derivative.

[9] Recent investigations of vapor pressures of solid and liquid Kr by Justi (see literature references at end of paper) agree with the results of Peters and Weil, whereas the results of Keesom, Mazur, and Meihuizen on vapor pressures of solid Kr disagree notably for the vapor pressure at the melting point.

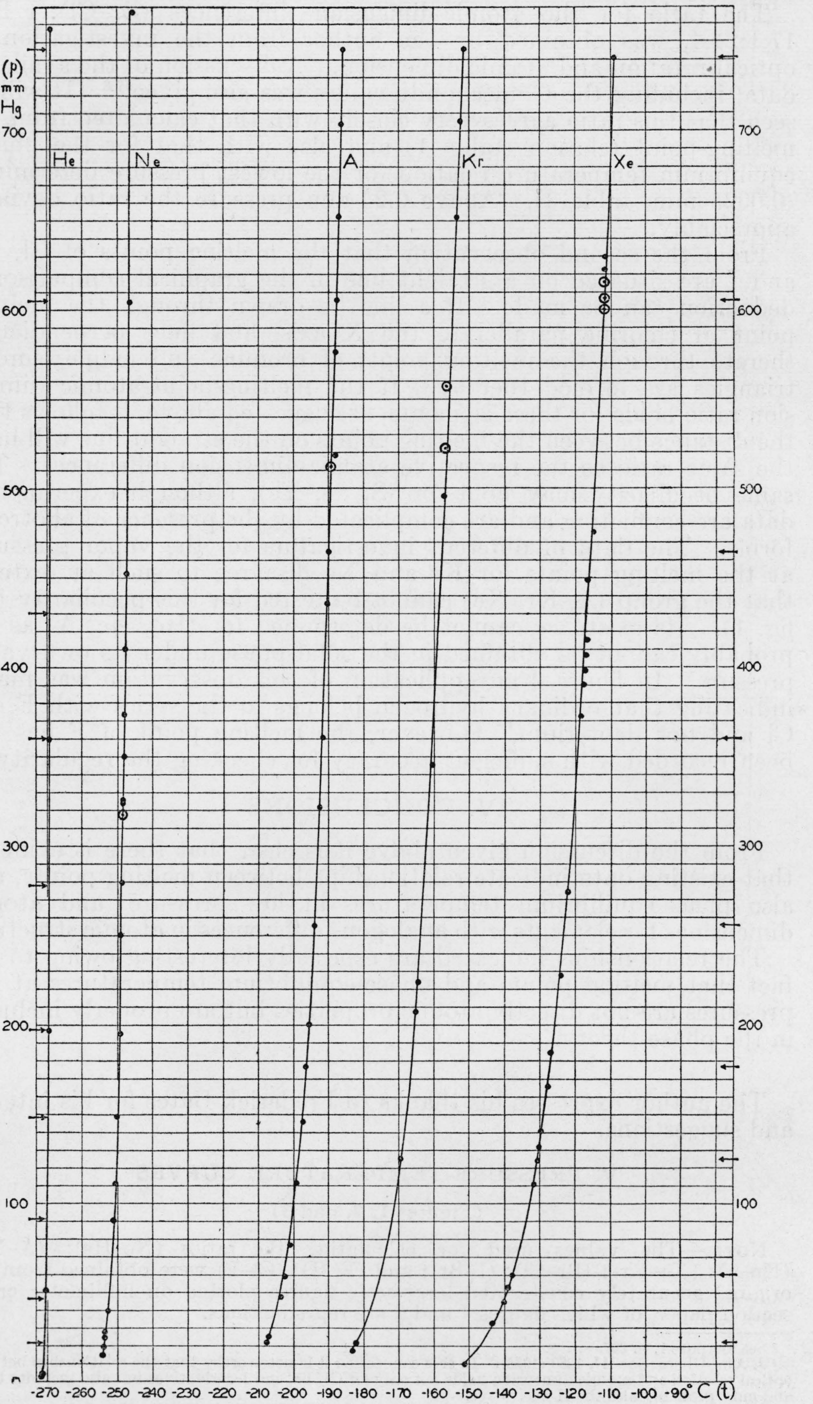

FIGURE 1.—*Pressure-temperature curves for* He, Ne, A, Kr, *and* Xe.

KEY (figs. 1, 2, and 3):

- ● Experimental data taken from the literature for constructing the *p–t* curves.
- ⊙ Melting points. (For references see tables 1, 2, and 3 and list of literatures on page 343–345 of this paper.
- → Pressures at which measurements were made.

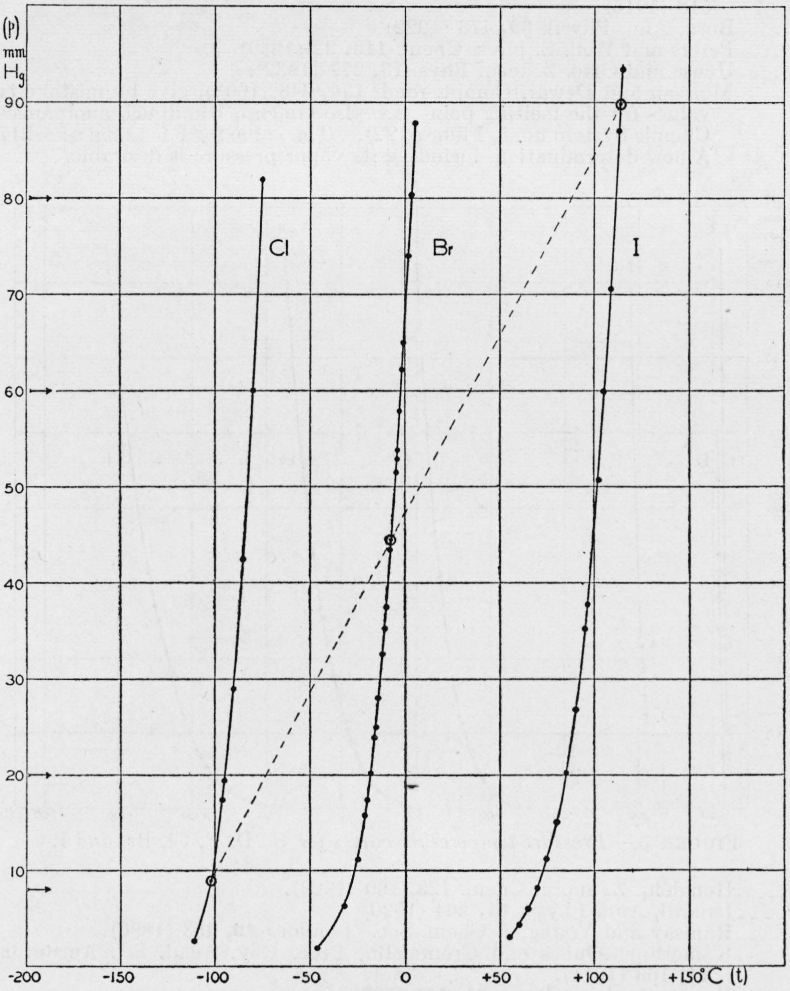

FIGURE 2.—*Pressure-temperature curves for* Cl, Br, *and* I, *from* 90 mm *of* Hg *to* *475* mm *of* Hg.

VI. LITERATURE FOR VALUES OF ATOMIC DIMENSIONS AND MELTING POINTS

1. ATOMIC DIMENSIONS

The values of Wherry (Am. Mineralogist **14,** 54; 1929) of the neutral (not ionized) atoms are given. These values are compiled from Goldschmidt (Die Gesetze der Krystallochemie, Skr. Norske Vidensk. Akad. Oslo **I,** Mat. Nat. Kl. No. 2, 117; 1926) and Pauling (J. Am. Chem. Soc. **49,** 765; 1927). The atomic radius of H$=(0.5285 \pm 0.004)\times 10^{-3}$ (Birge, Phys. Rev., Supp. 1; 1929). Jeans' Dynamic Theory of Gases (p. 152, 1916) gives H_r=atomic hydrogen= 0.502A to 0.63A; Bergmann and Engel (Z. phys. Chem. **13,** 247) for the radius of hydrogen in the vapor state, 0.48A.

2. MELTING POINTS

The value, as deemed most probable, is given, not an average of the most recent values.

He----Keesom, Proc. Roy. Acad. Amsterdam **29,** 1136 (1926).
Ne----Kamerlingh-Onnes and Crommelin, Proc. Roy. Acad. Sci. Amsterdam **18,** 518 (1916).
A-----Born, Ann. Physik **69,** 473 (1922).
Kr----Peters and Weil, Z. phys. Chem. **148,** 32 (1930).
Xe----Heuse and Otto, Z. tech. Phys. **13,** 277 (1932).
F-----Moissan and Dewar, Compt. rend. **136,** 643 (1903), give by mistake two values for the melting point (see also Gmelin, Handbuch anorganische Chemie System no. 5, Fluor p. 22). The value for F is taken as −217°. A new determination, including its vapor pressure is desirable.

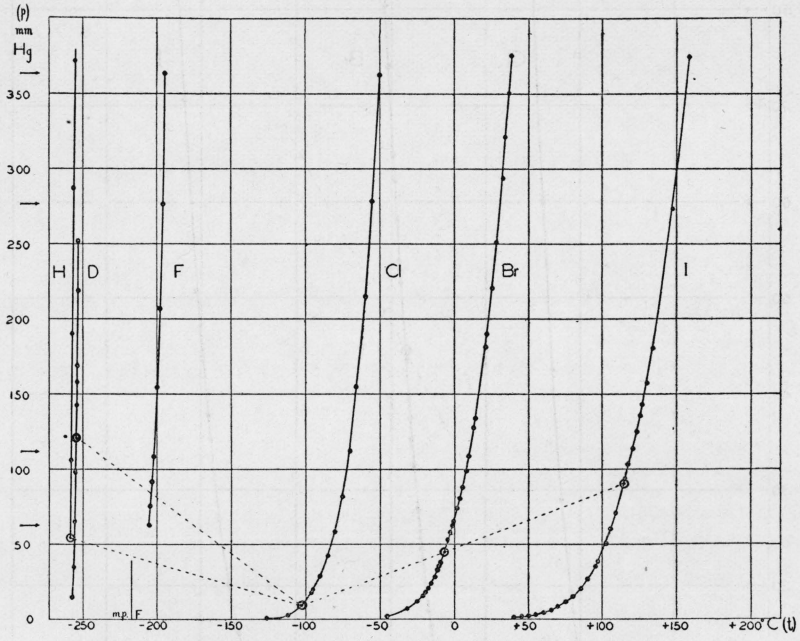

FIGURE 3.—*Pressure-temperature curves for* H, D, F, Cl, Br, *and* I.

Cl-----Henglein, Z. anorg. Chem. **123,** 160 (1923).
Br----Isnardi, Ann. Physik **61,** 264 (1920).
I------Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886).
O-----Kamerlingh-Onnes and Crommelin, Proc. Roy. Acad. Sci. Amsterdam **14,** 163 (1911).
S------Kruyt, Z. phys. Chem. **64,** 561 (1908).
Se-----Berger, Z. anorg. Chem. 85, 114 (1914).
Te----Damiens, Ann. chim. phys. [9] **19,** 44 (1923).

VII. LITERATURE FOR DATA ON p–t AND MELTING-POINT CURVES

He (*p–t*)--------Kamerlingh-Onnes and Weber, Proc. Roy. Acad. Sci. Amsterdam **18,** 505 (1915).
He (mp curve)---Keesom, Proc. Roy. Acad. Sci. Amsterdam, **29,** 1136 (1926). Simon, Edwards, and Ruhemann, Z. Elektrochem. **35,** 618 (1929). See also note and formula, Z. phys. Chem. [B] **6,** 338 (1929).
Ne (*p–t*)--------Crommelin and Gibson, Proc. Acad. Sci. Amsterdam **30,** 364 (1927).
Ne (mp curve)---Simon, Edwards, and Ruhemann, Z. phys. Chem. [B] **6,** 331 (1929).

A (*p–t*)---------Born, Ann. Physik **69,** 473 (1922).

A (mp curves)---Simon, Edwards, and Ruhemann, Z. phys. Chem. [B] **6,** 331 (1929).

Kr (*p–t*)--------Peters and Weil, Z. phys. Chem. **148,** 32 (1930). Justi, Phys. Z. **36,** 571 (1935). Keesom, Mazur, Meihuizen Physica **2,** 669 (1935).

Xe (*p–t*)--------Heuse and Otto, Z. tech. Phys. **13,** 277 (1932). Peters and Weil, Z. phys. Chem. **148,** 32 (1930). Allen and Moore, J. Am. Chem. Soc. **53,** 2522 (1931).

Cl (*p–t*)---------Henglein, Rosenberg, and Muchlinski, Z. Phys. **11,** 1 (1922) Pellaton, J. chim. phys. **13,** 440 (1915).

Br (*p–t*)---------Henglein, Rosenberg, and Muchlinski, Z. Phys. **11,** 1 (1922). Isnardi, Ann. Physik **61,** 264 (1920). Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886). The value +0.31° C for 65.0 mm of Hg (p. 456, series I) must be −0.31° C See on p. 455: −0.31° C at 65.25 mm; also Scheffer and Voogd, loc. cit., −0.42° C for 64.3 mm. Scheffer and Voogd, Rec. trav. chim. Pays Bas, **45,** 214 (1926).

I (*p–t*)----------Haber and Kerschbaum, Z. Elektrochem. **20,** 302 (1914). Baxter, Hickey, and Holmes, J. Am. Chem. Soc. **29,** 127 (1907). Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886).

H (*p–t*)---------Keesom, Byl, and van der Horst, Proc. Roy. Acad. Sci. Amsterdam **34,** 223 (1931).

D (*p–t*)---------Brickwedde, Scott, Urey, and Wahl, J. Chem. Phys. **2,** 456 (1934).

F (*p–t*)---------Claussen, J. Am. Chem. Soc. **56,** 614 (1934).

WASHINGTON, July 24, 1936.