that it may be possible to employ these reactions to make precise determinations of the ratios of equivalent weights, *e. g.*, the ratio Bi:3Ag. These displacement reactions should also prove useful as a convenient means of purifying some of the elements.

THE RICE INSTITUTE
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The Critical Constants of the Inert Gases and of Hydrogen Compounds Having the Same Number of Electrons per Molecule

BY GEORGE WOOLSEY

The values of the critical constants of pure substances are of fundamental importance in working with reduced equations of state. An error in any one of the three critical quantities, temperature, pressure or volume, introduces an inaccuracy in the value of $n(Rt_c/p_cv_c)$ which is used in the reduced equation in place of the gas constant, R. Hitherto almost no relationships have been found between the values of n for different substances which could serve, first, as a guide to the correctness of measured critical constants, and, second, as a means of estimating the value of n when only critical temperature and pressure have been measured. A study of the normal paraffin hydrocarbons has shown that n increases slightly with the size of the molecules except possibly in the case of the first few members of the series.

Another relationship between critical constants has been found in the case of the rare gases and of hydrogen compounds containing the same number of electrons per molecule as do the rare gases. The equation $n = Rt_cd_c/p_cM$ can be considered to be, except for variations in the value of n, the equation of a straight line passing through the origin when d_c/M is plotted against p_c/t_c. These substances and their critical values as plotted in Fig. 1 are listed in Table I.

Unfortunately, critical data are not complete for all of the substances of any of these groups except in the case of the one containing only helium and hydrogen. However, they are nearly enough complete in the neon and argon groups to make fairly reliable estimates, in the following manner.

Critical molecular densities are nearly linear with respect to number of hydrogen atoms in the case of the first, third, fourth, and fifth substances of the neon group and also for the first, second, and fourth substances of the argon group. This seems to indicate that linearity may be assumed so that the critical molecular densities of hydrogen fluoride, hydrogen sulfide and silicane can be estimated. Critical molecular densities are expressed in moles per liter ($1000\ d_c/M$). The estimated values are included, in parentheses, in Table I.

TABLE I

CRITICAL CONSTANTS OF THE INERT GASES AND OF HYDROGEN COMPOUNDS HAVING THE SAME NUMBER OF ELECTRONS PER MOLECULE

Period	Substances	Mol. wt.	t_c, °K.	p_c, atm.	d_c, g./cc.	p_c/t_c	$\frac{1000d_c}{M}$	n	Dipole moment $u \times 10^{18}$
0	Helium	4.00	5.19	2.161	0.06930	0.435	17.33	3.261	0
	Hydrogen	2.0155	33.25	12.80	.03102	.385	15.39	3.280	0
1	Neon	20.183	44.45	26.86	.4835	.605	23.96	3.245	0
	Hydrogen fluoride	20.01			(.416)	(.41)	(20.8)	(4.16)	
	Water	18.02	647.3	218.17	.3127	.337	17.36	4.226	1.85
	Ammonia	17.03	406.1	112.3	.234	.276	13.73	4.068	1.50
	Methane	16.03	191.1	45.8	.1615	.239	10.07	3.448	0
2	Argon	39.94	150.7	47.996	.53078	.319	13.30	3.424	0
	Hydrogen chloride	36.46	324.7	81.6	.424	.252	11.63	3.796	1.03
	Hydrogen sulfide	34.08	373.5	88.9	(.351)	.238	(10.2)	(3.52)	0.95
				(84.0)	(.351)	(.225)	(10.2)	(3.72)	
	Phosphine	34.04	324.2	64	.30	.197	8.82	3.66	0.55
	Silicane	32.09	269.6	48	(.234)	.178	(7.3)	(3.46)	
3	Krypton	83.70	210	54	.78	.257	9.32	2.98	0
	Hydrogen bromide	80.92	363.1	84		.232			0.78
	Hydrogen selenide	81.22	411.1	88		.214			
4	Xenon	131.3	289.8	58.22	1.154	.201	8.79	3.590	0
	Hydrogen iodide	127.93	424.1	82		.194			
5	Radon	222.0	377	62		.165			

Next, the values of p_c/t_c for the substances in each group were plotted against the number

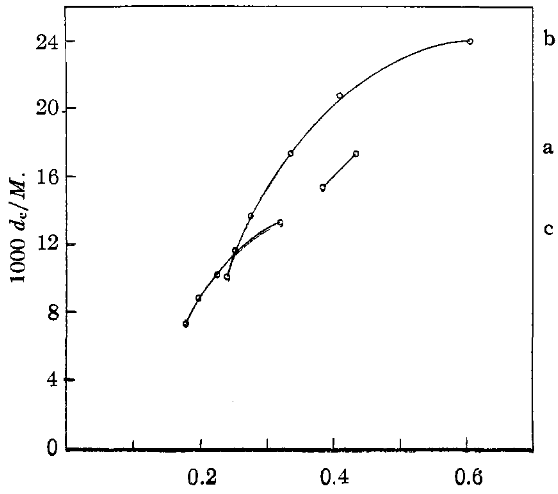

Fig. 1.—Groups: a, helium; b, neon; c, argon.

of hydrogen atoms, and all known values but that of hydrogen sulfide fall into a consistent series of curves.

This seems to indicate that the reported value for hydrogen sulfide is incorrect. In order to place it on the curve it is necessary to assume that its critical pressure is 84 atmospheres instead of the reported 88.9 atmospheres, critical temperature being assumed correct. Using these curves the unknown value for hydrogen fluoride is interpolated.

From these estimates values of n were computed and then the critical molecular densities were plotted against p_c/t_c in Fig. 1.

It will be noticed that the neon and argon groups each begin with an inert gas (non-polar), then include three polar substances, and are completed with a non-polar substance. From the relationships just discussed it would seem safe to assume that the critical molecular density is but little affected by the polarity of any substance. The effect of polarity is seen in the reduction of the values of p_c/t_c (atmospheres per degree) for polar substances with the resultant increase in the value of n.

VALENCIA HIGH SCHOOL
PLACENTIA, CALIF.
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COMMUNICATIONS TO THE EDITOR

THE ISOTOPES OF POTASSIUM AND LITHIUM IN SARATOGA MINERAL WATER AND CRYPTOZOON

Sir:

The abundance ratio for the isotopes of potassium in ocean water and in most minerals has been shown to be K^{39}/K^{41} = 14.20 to 14.25 [Brewer, THIS JOURNAL, **58,** 365–370 (1936)]. Kelp and agar, in comparison to ocean water, possess an appreciably higher concentration of K^{41}. Since no significant deviation from the average has been detected in the large number of rocks and minerals investigated, it was felt that it would be of interest to test the isotope ratio in old mineral formations of presumably marine plant origin

The most prevalent organism of the Ozarkian period (upper Cambrian time) was calcareous (lime secreting) algae or seaweed grown half a billion years ago, known as Cryptozoon [H. P. Cushing and R. Ruedemann, New York State Museum Bull. 169 (1914); R. T. Colony, Legislative Document No. 70 (1930); Oskar Baudisch, "Comparative Spectroscopic Studies of *Cryptozoon proliferum* and the Mineral Springs of Saratoga Springs, N. Y."]. These very striking and spectacular fossils are exposed as reef beds in the Saratoga area in New York. What we see here today is a portion of the old sea-bottom elevated into land area. In the shallow warm water of the Cambrian sea grew the multitudinous colonies of Cryptozoon and seaweed. Accordingly, tests have been made of the abundance ratio of isotopes of potassium, lithium and rubidium in these formations as well as the overlying shale and the Saratoga Springs mineral waters.

The K^{39}/K^{41} abundance ratios from the rocks and waters tested are given in Table I.

The results just presented show an appreciable concentration for K^{41} in the mineral water and