Examination of the table leads to the following conclusions: (1) The CH_2 group is structurally equivalent to ether O, and the CH group is structurally equivalent to tertiary N. (2) The CH_3 group is not equivalent to NH_2 or OH, nor is CH_2 equivalent to NH, since hydrogen bond formation is possible when H is attached to N or O. (3) The CH_2 group is not equivalent to ketone O, nor is CH equivalent to nitrile N.

The abnormality of liquids containing $C{=}O$ or $C{\equiv}N$, as shown by this boiling point criterion and also by other criteria, is much less than that of liquids containing hydrogen bonds, and so these liquids are put into an intermediate classification. The abnormal character must arise from the interaction of the $C{=}O$ or $C{\equiv}N$ polar groups, which are quite strongly polar and occupy exposed positions on the molecules.

Conclusion (1) is to be expected since CH_2 and O, and CH and N, have nearly the same mass and electronic structures, and the bond angles around C, N and O are probably the same. This structural equivalence does not appear to hold in aromatic compounds since pyridine has a much higher viscosity and boiling point than benzene.

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Displacement Reactions in Fused Pyridinium Hydrochloride Solutions

By Arthur F. Scott and Clarence S. Coe

Fused pyridinium hydrochloride has been shown[1] to act both as an "onium" acid and as an ionizing solvent for salts of metals. As an acid, pyridinium hydrochloride dissolves metals above hydrogen in the electromotive series; it also dissolves copper readily, but it does not attack antimony, bismuth or arsenic, even though these elements are above copper in the series. Since this apparently irregular position of copper is the same as it is in the electromotive series of metals[2] in solvents of fused aluminum bromide and zinc bromide, it appeared possible that the series for pyridinium hydrochloride is in general like the abnormal series found with the other fused salts. To test this possibility we have attempted to establish the series for pyridinium hydrochloride by means of displacement reactions.

Weighed amounts of different metals were added to melts of various metallic chlorides in pure pyridinium hydrochloride. The molecular concentration[3] of the chlorides in the melt was about 1 *M*, the extreme variations being 0.5 and 1.9 *M*. The amount of the metal added was approximately equivalent to two-tenths of the metal in the melt. The time allowed for the reaction varied between fifteen minutes and one hour, depending on how rapidly the reaction appeared to take place. Finally, after the melt was cooled, the metallic residue was recovered and its weight ascertained. As a rule, in order to facilitate the separation of the metallic residue from the solid pyridinium hydrochloride solution, the latter was treated with hot water or hydrochloric acid solution.

Complete, *i. e.*, more than 95% displacement took place as follows: gold, by mercury, bismuth and antimony; arsenic, by mercury and bismuth; mercury, by antimony; bismuth, by antimony and silver. Partial, *i. e.*, 95–50% displacement took place as follows: mercury, by bismuth and by silver, and antimony by silver. Gold was not displaced by platinum, nor mercury by arsenic, nor bismuth by mercury, nor antimony by mercury.

On the basis of these reactions and that of copper with pyridinium hydrochloride we may write the displacement series for metals in pyridinium hydrochloride as in (I) below. The series for these metals in fused zinc bromide and fused aluminum bromide as found by Isbekow[2] from measurements of the decomposition potentials as well as from displacement reactions is given in (II).

(I)	Cu	H	Ag		Sb	Bi	Hg	As	Au	Pt
(II)	Cu		Ag	Hg	Sb	Bi				

On comparing these two series it can be seen that the series for pyridinium hydrochloride differs from that for fused zinc bromide and aluminum bromide only in the position of Hg. Both of these series (I and II) differ from the usual series in that Cu and Ag are above Sb, Bi and As. From the fact that Cu in the pyridinium chloride is above H it would appear that the abnormal sequence is due to a displacement of Cu, Ag and possibly Hg and Au.

In conclusion, it may be noted that some of the displacement reactions in pyridinium chloride which go to completion may be of practical value. For instance, preliminary experiments indicate

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[1] Audrieth, Long and Edwards, This Journal, **58**, 428 (1936).

[2] Isbekow, *Z. physik. Chem.*, **116**, 304 (1925); *Z. anorg. Chem.*, **185**, 324 (1930).

[3] The concentration of the auric chloride was small but not determined. The solutions of arsenic were prepared by dissolving arsenous oxide.

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.

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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			