alkylated benzenes have been reported.[11] The absorbance values[12] for the charge-transfer band of hexamethylbenzene were recalculated by our method and plotted in Fig. 4. Values of K_x = 15.3 ± 0.3 and ϵ_c = 6,600 ± 400 were obtained as compared with values of K_x = 15.24 and ϵ_c = 6,690 reported by Tamres, *et al.*

The equilibrium between hexaethylbenzene and iodine was re-examined and the data are plotted in Fig. 3. The data show extremely good precision. However, the conditions chosen were such that the slopes of the K *vs.* ϵ_0 lines were all very much alike. If one evaluates the accuracy of the results considering the reported reproducibility of the absorption values (*i.e.*, 0.01), intersections in the region K = 3 to 7 are possible (Fig. 5). The equilibrium constant is lower than that for hexamethylbenzene but is not accurately known. This problem was also investigated by Keefer and Andrews but neither absorbance values nor base concentrations were reported so the data could not be evaluated. A re-evaluation of the accuracy of the ΔH measurement by Keefer and Andrews is desirable to establish the cause of the difference between hexaethyl- and hexamethylbenzene.

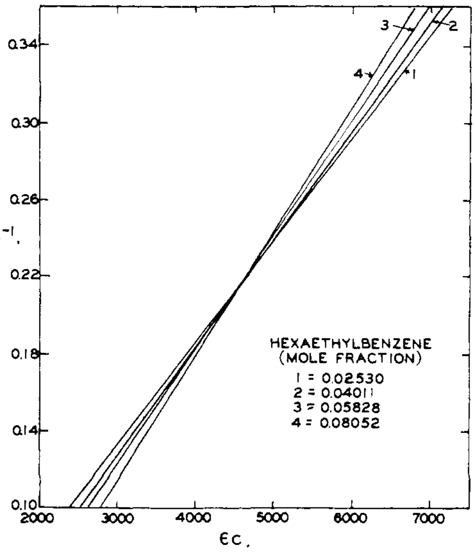

Fig. 5.

URBANA, ILLINOIS

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(11) M. Tamres, D. R. Virzi and S. Searles, THIS JOURNAL, **75**, 4359 (1953).

(12) D. R. Virzi, B.S. Thesis, University of Illinois, 1952.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogen Bonding Studies. II.[1] The Acidity and Basicity of Silanols Compared to Alcohols[2]

BY ROBERT WEST AND RONALD H. BANEY

RECEIVED MAY 18, 1959

The hydrogen bonding acidity and basicity of some silanols and carbinols has been determined by the measurement of O–H stretching infrared band shifts[3] upon admixture with the bases ether and mesitylene, and the acid phenol, respectively. The silanols studied are much more strongly acidic, but only slightly less basic, than the carbinols with analogous structure. The results for the silanols are discussed in terms of a model with strong π-bonding from oxygen to silicon involving only one of the two unshared electron pairs on the silanol oxygen. Intermolecular association of silanols also was studied by infrared spectroscopy. Trimethyl- and triethylsilanol are somewhat more associated than the corresponding carbinols, and the hydrogen bonds formed between silanol molecules appear to be decidedly stronger than those involving alcohols.

Organosilicon hydroxides (silanols) have been known since the first preparation of triethylsilanol by Ladenburg in 1871,[4] but only in recent years has any attempt been made to compare the properties of silanols with those of their purely organic analogs, the carbinols, in any direct or quantitative manner. In 1946 Sommer, Pietrusza and Whitmore showed that trimethylsilanol is converted to its sodium salt by 12 N NaOH and commented on the increased reactivity of the hydroxyl proton in silanols compared to alcohols.[5] More recently Allred, Rochow and Stone have examined the n.m.r. spectrum of trimethylsilanol and found that the hydroxyl hydrogen is less shielded (more protonic) than that in *t*-butyl alcohol.[6] The reverse would be expected on the basis of the electronegativity and inductive effect of silicon[7] and these workers attributed the decreased shielding in the silanol to π-bonding involving p-electrons of oxygen and vacant 3d orbitals of silicon.[8]

The boiling points of silanols indicate that, like alcohols, they are associated by intermolecular hydrogen bonding. The apparent molecular weights of some silanols in cyclohexane solution have been determined by Grubb and Osthoff and found to be similar to those for the corresponding carbinols.[9] The infrared spectra of several sil-

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(1) R. West, THIS JOURNAL, **81**, 1614 (1959), will be regarded as the first paper in this series.

(2) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(3) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(4) A. Ladenburg, *Ber.*, **4**, 901 (1871); *Ann.*, **164**, 300 (1872).

(5) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946); L. H. Sommer, L. Q. Green and F. C. Whitmore, *ibid.*, **71**, 3253 (1949).

(6) L. Allred, E. G. Rochow and F. G. A. Stone, *J. Inorg. and Nuclear Chem.*, **2**, 416 (1956).

(7) R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953); L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951); C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954).

(8) F. G. A. Stone and D. Seyferth, *J. Inorg. and Nuclear Chem.*, **1**, 112 (1955).

(9) W. T. Grubb and R. C. Osthoff, THIS JOURNAL, **75**, 2230 (1953).

anols in the 2–15 μ region have been examined qualitatively by workers who have noted that absorption bands attributable to both free and associated hydroxyl vibrations could be identified in the silanol spectra.[10] Russian workers also have studied the Raman spectrum of pure liquid trimethylsilanol. The associated O–H stretching band extends to unusually low frequencies in the silanol, implying unusually strong hydrogen bonding, attributed to enhanced acidity of the silanol.[11]

The foregoing work suggested that a detailed examination of the infrared absorption of silanols in the OH stretching region might provide a clearer picture of electron distribution and bonding in these compounds. The objectives of our work were (1) to compare the relative acidity and basicity of silanols and carbinols in intermolecular hydrogen bond formation with other species, and (2) to compare the degree of association and strength of intermolecular hydrogen bonding of silanols with those of carbinols.

Experimental

Compounds.—The carbinols were all Eastman Kodak white label materials which were purified by distillation or recrystallization. Pure samples of Me_3SiOH and Et_3SiOH kindly were donated by Dr. R. Anderson of the General Electric Company. Trimethylsilanol also was synthesized by the method of Sommer.[12] Triphenylsilanol was prepared by the alkaline hydrolysis of triphenylchlorosilane.[13] The physical constants of all of the carbinols and silanols agreed with those reported in the literature. Phenol, mesitylene and diethyl ether were reagent grade materials which were dried and fractionally distilled. Merck reagent grade carbon tetrachloride from freshly opened bottles was used as a solvent. The water content of this material was negligible, as shown by its lack of absorption in the 3700 cm.$^{-1}$ region.

Diphenylsilanol.—This new compound was synthesized from diphenylsilane by bromination and careful hydrolysis. To a solution of 41 g. (0.2 mole) of diphenylsilane in 200 ml. of carbon tetrachloride was added, over 2 hr., a solution of 32 g. (0.2 mole) of bromine in 100 ml. of CCl_4. The mixture then was heated to reflux for 1 hr. with stirring. The CCl_4 was evaporated under reduced pressure and the residue was distilled through a short Vigreux column under vacuum. The product was 40 g. of heavy oil, b.p. 131–138° (9 mm.), mostly diphenylbromosilane but containing some diphenyldibromosilane. Ten grams of the oil was dissolved in 100 ml. of ether and added slowly with rapid stirring to a mixture of 18 g. of NH_4Cl, 18 ml. of 12 *M* ammonia solution, 100 ml. of cold water and 100 ml. of ether. The ether solution was separated and evaporated under reduced pressure to 100-ml. volume. Pentane (400 ml.) was added, precipitating 2 g. of a white solid which was filtered off and identified as diphenylsilanediol. The filtrate was allowed to evaporate, yielding an oil which slowly underwent partial solidification to transparent crystals.

These were washed repeatedly with pentane, then taken up in a small volume of CCl_4 and recrystallized by slow evaporation to give 6 g. of product with m.p. 61.5–63°. The infrared spectrum showed bands attributable to O–H, Si–H, Si–O and Si-phenyl vibrations.

Anal. Calcd. for $C_{12}H_{12}OSi$: C, 71.9; H, 6.04; mol. wt., 200. Found: C, 71.9; H, 5.54; mol. wt., 182.

The residual oil from the initial crystallization of diphenylsilanol was combined with the pentane washings and the solution was allowed to evaporate. White crystals of the pentane-soluble condensation product 1,1,3,3-tetraphenyldisiloxane eventually formed; yield 3.2 g., m.p. 45.5–47.5°. (This compound was actually the normal product of the above reaction sequence, diphenylsilanol being obtained only twice in seven attempts.) The infrared spectrum showed bands attributable to Si–H, Si–O and Si–C_6H_5 but no O–H bands.

Anal. Calcd. for $C_{24}H_{22}OSi_2$: C, 75.4; H, 5.8. Found: C, 75.2; H, 5.8.

Spectra.—The extent of intermolecular association of silanols and alcohols was studied in the near infrared region using a Cary Model S Spectrometer with quartz optics. The absorbancies of the first overtone of the unassociated OH stretching band for each compound were plotted against concentration. Extrapolation to infinite dilution gave a straight line from which the molar absorbancy index for the compound could be obtained. Deviations from this straight line were taken as a measure of the extent of association at different concentrations (Table I).

TABLE I

BAND SHIFTS IN CM.$^{-1}$ AND % ASSOCIATION OF CARBINOLS AND SILANOLS

	Frequency free OH	$\Delta\nu$, "Dimer"	% Assoc. 0.5 *M*	% Assoc. 1.0 *M*	$\Delta\nu$, PhOH	$\Delta\nu$, Et_2O	$\Delta\nu$, Me_3Ph
Me_3COH	3616	120	52	66	271	122	47
Et_3COH	3616	119	19	35	262	118^a	48
Ph_3COH	3609	122			172^a	174	50
Ph_2CHOH	3614	139			201^a	177	45
Me_3SiOH	3688	189	68	81	216	238	71
Et_3SiOH	3685	185	49	66	228^a	230	62
Ph_3SiOH	3677	206			175^b	311^a	79
Ph_2SiHOH	3675	223^a			194^b	322^b	74
PhOH	3609	132			132	280	76

All $\Delta\nu$ values are ±4 cm.$^{-1}$, except for: ^{a} ±10 cm.$^{-1}$; ^{b} ±20 cm.$^{-1}$. The columns headed $\Delta\nu$, "Dimer," $\Delta\nu$, Et_2O, and $\Delta\nu$, Me_3Ph refer to frequency shifts of the carbinols and silanols; the column headed $\Delta\nu$, PhOH refers to frequency shifts of phenol bonded to the carbinols and silanols.

All other spectral measurements were made in the O–H fundamental region using a Perkin–Elmer Model 112 double-pass spectrometer equipped with a CaF_2 or LiF prism, calibrated with ammonia gas and water vapor. Assignments are believed correct to within ±2 cm.$^{-1}$ for sharp bands. Silanols and alcohols were present at 0.02 *M* in the mixtures with phenol and bases; at this concentration the contribution of dimer and polymer bands to the O–H absorption is negligible. Phenol was used at 0.02 *M*, ether at 0.25 *M* and mesitylene at 0.05 *M* in the mixtures with silanols and carbinols. Each mixture was run at 3 and 10 mm. path length in cells with NaCl windows. Spectra of the bases ether and mesitylene were run at the same concentration and point-by-point difference plots were constructed to eliminate any contribution of base to absorption in the O–H region (Fig. 1).

The "dimer" peaks were taken at silanol or carbinol concentration of 0.05 *M*. The positions of the "dimer" peaks were shown not to vary significantly over the range 0.02–0.1 *M* for the compounds studied.

Discussion

Acidity and Basicity of Silanols.—The acidity of the silanols and carbinols as hydrogen donors in hydrogen-bond formation was measured by the shift of the O–H stretching band on hydrogen bonding to the bases ether and mesitylene (Fig. 1). Data are summarized in Table I. Badger has shown that $\Delta\nu$ is approximately proportional to ΔH for hydrogen-bonding reactions involving

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[10] (a) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949); (b) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952); (c) M. Kakudo, P. N. Kasai and T. Watase, *J. Chem. Phys.*, **21**, 1894 (1953); (d) V. I. Kasatochkin, M. I. Shostakovskii, O. I. Zil'berbrand and D. A. Kochkin, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **18**, 726 (1954).

[11] M. I. Batuev, M. F. Shostakovskii, V. I. Belyaev, A. D. Matveeva and E. V. Dubrova, *Doklady Akad. Nauk S.S.S.R.*, **95**, 531 (1954).

[12] L. H. Sommer, E. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946).

[13] W. C. Schumb and C. M. Saffer, Jr., *ibid.*, **61**, 363 (1939).

hydroxyl compounds.[14] The proportionality constant between $\Delta\nu$ and ΔH may be somewhat different for silanols than for alcohols, but we believe that these band shift values should indicate qualitative trends in the strength of the hydrogen bonds. On association to the base diethyl ether, the silanols give band shifts nearly twice as great as do the corresponding carbinols, indicating that the silanols are much more acidic than the carbinols. The presence of phenyl rings bonded to the central atom markedly increases the acidity of both silanols and carbinols toward ether, so that the $\Delta\nu$ values decrease in the order arylsilanols > alkylsilanols > arylcarbinols > alkylcarbinols. The differences between the two compounds in each of these four classes are small indicating that steric factors are of little importance in determining $\Delta\nu$. The $\Delta\nu$ values for hydrogen bonds to mesitylene show the same trends, although the differences are not as large. It is of special interest that the arylsilanols appear to be about as acidic in hydrogen bond formation as the strongly acidic alcohol, phenol.

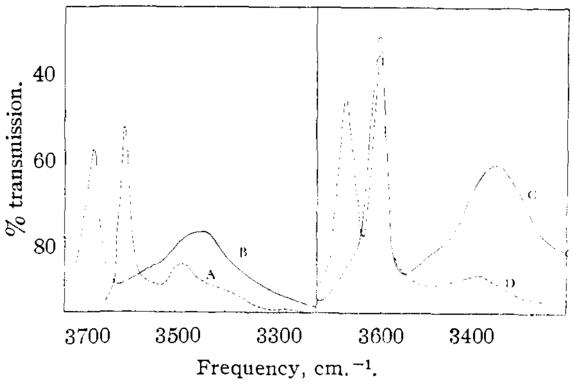
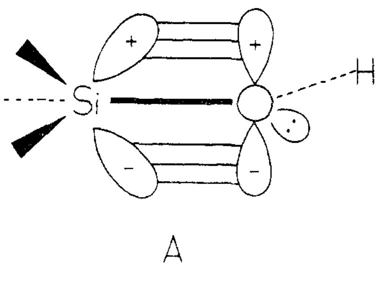


Fig. 1.—Infrared spectra of mixtures of hydroxyl compounds with ether (left) and phenol (right) in carbon tetrachloride at 25°: A, 0.02 M $(CH_3)_3COH$ and 0.25 M $(C_2H_5)_2O$; B, 0.01 M $(CH_3)_3SiOH$ and 0.25 M $(C_2H_5)_2O$; C, 0.02 M $(CH_3)_3COH$ and 0.01 M C_6H_5OH; D, 0.01 M $(CH_3)_3SiOH$ and 0.01 M C_6H_5OH. Curves A and B are difference plots with the absorption of 0.25 M $(C_2H_5)_2O$ alone subtracted. Slit width is 85 μ.

Our results corroborate the chemical and n.m.r. evidence for the enhanced acidity of silanols summarized in the Introduction[5,6] and show that this acidity is reflected in strong intermolecular hydrogen bond formation by the silanols. The fact that arylsilanols give band shifts as large as phenol led us to determine the strength of triphenylsilanol as a Brønsted acid, by direct potentiometric titration. Our preliminary results show that in the solvent pyridine, triphenylsilanol is weaker than phenol, although it is of the same order of magnitude of acid strength.[15]

The basicity of the silanols and alcohols toward hydrogen bond formation was measured by the shift of the OH band of phenol on hydrogen bonding to the hydroxyl compound (Fig. 1, Table I).[16] Triethylcarbinol is a slightly stronger base than t-butyl alcohol, indicating that steric factors are again unimportant. The order of decreasing basicities is alkylcarbinols > alkylsilanols > arylcarbinols ~ arylsilanols. Among the alkyl substituted compounds, for which the data are better, the carbinols give band shifts only about 20% greater than the silanols. The $\Delta\nu$ values for the arylsilanols are hard to measure because of competing hydrogen bonding by the acidic silanol O–H, but any differences in basicity between these compounds and the arylcarbinols seem to be small. Our conclusion is that silanols, despite their greatly enhanced acidity, are *nearly as strong bases as carbinols*.

The hydrogen bond acidity and basicity for a hydroxyl compound need not be complementary since the acidity and basicity of the same species is being measured, rather than the acidity and basicity of a conjugate acid and base. However, previous work by Kuhn[3] indicates that for a number of alcohols, basicity bears an inverse relationship to acidity. It is remarkable, then, that the greatly enhanced acidity of silanols is not offset by a corresponding decrease in basicity. We believe that, as others have suggested, the increased acidity of silanols is due to π-bonding involving unshared electrons of oxygen and an unfilled d orbital of silicon, increasing the positive character of the proton.[6,8] It remains to be explained why the resulting drift of electrons away from oxygen does not reduce the basicity of the silanols to the same extent. If the oxygen in silanols is considered to have bond hybridization sp^2, with an unshared pair occupying one of the hybrid orbitals and sigma-bonds to Si and H the other two, the remaining electron pair in a p orbital can overlap with a 3d orbital of silicon (model A). The trigonal oxygen in the model A would be in a somewhat similar electronic situation to the nitrogen atom in an imine ($R_2C{=}N{-}H$). It should have substantial basic properties by virtue of its single remaining unshared pair of electrons in the sp^2 orbital.



A

An alternative model is possible involving a linear Si–O–H system with sp hybridization at oxygen, and π-bonding involving both of the unshared pairs on oxygen with 3d silicon orbitals. The Si–O–H bond angle is not known directly, but the linear structure seems unlikely in view of the

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[14] R. F. Badger, *J. Chem. Phys.*, **8**, 288 (1940); R. F. Badger and S. H. Bauer, *ibid.*, **5**, 839 (1937); *cf.* C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

[15] R. West and R. H. Baney, *J. Inorg. and Nuclear Chem.*, **7**, 297 (1958).

[16] Phenol is sufficiently more acidic and less basic than the carbinols and alkylsilanols that the alternate process, hydrogen bonding of the carbinols or alkylsilanols to phenol, does not occur to any significant extent under the conditions of concentration used. The arylsilanols are acidic enough so that some hydrogen bonding to phenol does take place, complicating the infrared spectra. As a consequence the band shifts for association of phenol to arylsilanols are known less accurately.

positions of the Si and O atoms in crystals of dialkylsilanediols.[17] If the linear (sp) structure were correct, one would expect greatly decreased basicity, since in hydrogen bond formation π-electrons are much less basic than unshared pairs.[18] Pi-bonding involving both electron pairs of oxygen may be important in the nearly linear siloxanes[19] and perhaps also in silanolate ions.

Intermolecular Association of Silanols and Carbinols.—Data on the degree of association also are summarized in Table I. The fraction associated was determined by the deviation from Beer's law with increasing concentration shown by the first overtone of the non-bonded OH absorption.[20]

Only the alkyl substituted silanols and carbinols were sufficiently soluble in CCl_4 to permit measurement of the degree of association. Among these compounds, the silanols are somewhat more associated than the carbinols at any given concentration, but the differences are not large (Table I). The differences between the triethyl and trimethyl compounds in either series are as large as the difference between, *e.g.*, trimethylsilanol and trimethylcarbinol. This suggests that steric factors are very important in determining the degree of association and that decreased hindrance alone might explain the enhanced association of the silanols.

As the concentration of an alcohol in an inert solvent is increased, the first absorption band to appear at lower frequency is by common consent attributed to the O–H vibrations in the hydrogen-bonded dimer, while the broad band appearing at higher concentration and still lower frequency is attributed to higher polymers.[21,22] The silanols, like alcohols, develop two lower-frequency OH bands as the concentration is increased. The position of the first low-frequency band for the compounds studied is given in Table I in the "dimer" column, in terms of the frequency difference ($\Delta\nu$) between this band and the non-bonded OH absorption. There is as yet no firm evidence that the nature of the species responsible for the first low frequency band is the same for alcohols and silanols. However, it is interesting to note that the hydrogen bonds in this first associated species appear to be substantially stronger for silanols than for carbinols. This confirms Batuev's observation that the band shift on polymer formation in trimethylsilanol is exceptionally large.[11] Particularly strong hydrogen bonds in the associated species would be expected for the silanols if they are much more acidic but only slightly less basic than alcohols.

The frequency of the free O–H absorption band of the silanols studied is significantly higher than the free O–H band for alcohols. The silanols absorb in the region 3675–3688 cm.$^{-1}$ while the carbinols absorb at 3600–3614 cm.$^{-1}$. Carbinols generally absorb in the region 3605–3645 cm.$^{-1}$.[23] Batuev and his co-workers previously have noted the high frequency of the free O–H vibration in trimethylsilanol and attributed this shift to enhancement of the O–H bond force constant by the electropositive silicon atom.[11] Pi-bonding from oxygen to silicon, and the probably larger Si–O–H bond angle, may also influence the position of the O–H absorption and at present the evidence seems to us insufficient to explain the phenomenon.

Acknowledgments.—The authors are indebted to Miss Karen J. Lake for her patient assistance with the preparation of diphenylsilanol.

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[17] M. Kakudo and T. Watase, *J. Chem. Phys.*, **21**, 167 (1953); *Bull. Chem. Soc. Japan*, **27**, 605 (1954); M. Kakudo, N. Kasai and T. Watase, *J. Chem. Phys.*, **21**, 1894 (1953).

[18] M. Tamres, THIS JOURNAL, **74**, 3375 (1952); R. West, *ibid.*, **81**, 1614 (1959).

[19] R. C. Lord, D. W. Robinson and W. C. Schumb, *ibid.*, **78**, 1327 (1956); *cf.* R. F. Curl, Jr., and K. S. Pitzer, *ibid.*, **80**, 2371 (1958).

[20] If the nature of the association reactions were known, our spectral measurements would permit calculations of the equilibrium constants for these reactions.[21] In the absence of definite knowledge about the nature of the association reaction in silanols and carbinols, we have preferred to leave our data in the form of per cent. association at several concentrations. These figures should be directly comparable for silanols and carbinols.

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[22] F. A. Smith and G. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 151 (1951).

[23] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, 1958, p. 97.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ST. LOUIS UNIVERSITY]

Reactions between Dry Inorganic Salts. X. The Effect of Rubidium Chloride on the Transition Temperature of Cesium Chloride

BY LYMAN J. WOOD, CHAS. SWEENEY, S.J.,[1] AND SR. M. THERESE DERBES[1]

RECEIVED APRIL 20, 1959

A study of the effect of rubidium chloride on the transition temperature of cesium chloride has been made by means of the high temperature X-ray camera. It has been established that increasing amounts of added rubidium chloride cause a spectacular lowering of the transition temperature and that, at room temperature, up to 30 mole % of the high temperature form of cesium chloride may remain in the rubidium chloride in the form of a solid solution.

In a previous publication[2] it was shown that addition of cesium bromide to cesium chloride raises markedly the temperature at which the Pm3m→Fm3m transition begins and that the

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[1] Taken in part from theses presented to the faculty of St. Louis University for the degree of Master of Science.

[2] L. J. Wood, Wm. Secunda and C. H. McBride, THIS JOURNAL, **80**, 307 (1958).