

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

Equilibrium between Ammonia and Hydrogen Selenide

BY F. F. MIKUS AND F. J. POSS¹

The equilibrium between ammonia and hydrogen sulfide was thoroughly investigated by Isambert² and Magnusson.³ A careful survey of the literature revealed no quantitative data on the equilibrium between ammonia and the analog of hydrogen sulfide, hydrogen selenide, but merely a statement that the decomposition pressure of ammonium hydroselenide is small. In this work the equilibrium constants for the dissociation of ammonium hydroselenide according to the reaction, $\text{NH}_4\text{HSe(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{Se(g)}$, have been determined in the temperature range of 15 to 30.1°.

Experimental

Hydrogen Selenide.—Hydrogen selenide was prepared in an evacuated flask by dropping freshly boiled water upon a large excess of aluminum selenide which had been prepared by the ignition of an intimate mixture of one part powdered aluminum and two parts selenium. Drying of the gas was effected by the excess aluminum selenide. The hydrogen selenide was used immediately upon preparation, and the purity was determined at the time the sample was withdrawn for use.

Ammonia.—Ammonia was prepared by warming C. p. ammonium hydroxide and by passing the resultant gas through four drying towers containing soda lime, potassium hydroxide pellets, soda lime, and potassium hydroxide pellets plus metallic sodium, respectively. The effluent gas, when absorbed in sulfuric acid, always contained less than 0.4% unabsorbable gas.

Determination of the Equilibrium Pressure.—The apparatus (Fig. 1) used for the determination of the equilibrium pressure, when the excess hydrogen selenide or ammonia was expelled, consisted of two Hempel burets set parallel to each other and connected with glass tubing. These were surrounded by water jackets. The temperature was maintained constant to within 0.05° by circulating water from a constant temperature bath by means of a centrifugal pump. The temperature of the room was kept slightly higher than that of the water-bath. The mercury levels were read by means of a cathetometer placed at a distance of eight feet from the apparatus.

Ammonia and hydrogen selenide were brought together in buret B with the formation of a white crystalline solid on the inner surface. The excess gas was expelled by pushing the gas into the evacuated portion E F and pumping out through G. Buret C was evacuated with a Hyvac pump, and the leveling bulb D was adjusted to leave from 10 to 40 ml. of evacuated space above the mercury. The stopcocks, E and F, were turned to allow the gas formed from the dissociation of the ammonium hydroselenide to expand into buret C. The difference in the height of the mercury in this buret before and after expansion gave the equilibrium pressure. The second reading was corrected for the change in the level of the mercury in the leveling bulb. Equilibrium was attained rapidly; no change in pressure was noted after two minutes.

An advantage of the system employed lay in the fact that it was not necessary to consider barometric pressure in the measurements. Furthermore, since the second buret was not coated with ammonium hydroselenide the

adsorption of ammonia was minimized. As a result, pressure readings were more easily reproduced than in the system using one buret. When excesses of either of the gases were used, the two buret system was not used. Here it was necessary to measure the total volumes of the gases, which was done more conveniently when one buret was used. All measurements were made according to the method of Magnusson.³

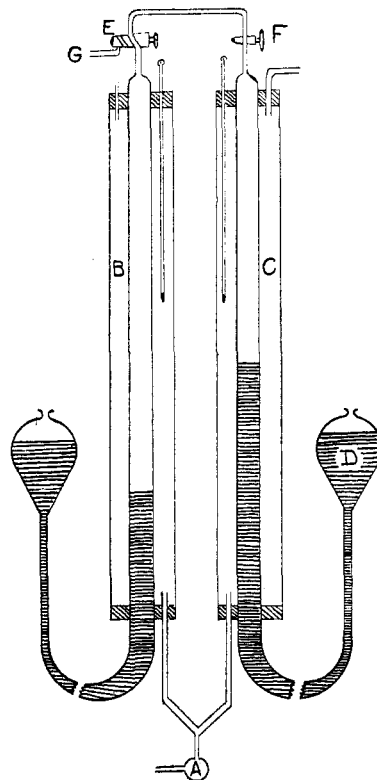


Fig. 1.

Analysis of NH_4HSe .—Considerable difficulty was encountered in attempting to analyze the white crystalline solid formed upon treating hydrogen selenide with ammonia. Traces of air coming in contact with the solid caused decomposition. A stoichiometric relationship between the two gases forming the solid was obtained by slowly introducing hydrogen selenide into a measured amount of ammonia in a buret until no decrease in volume of the gas in the buret was observed. Further addition of hydrogen selenide caused an increase. The hydrogen selenide was 93.4% pure.

Data and Discussion

Table I shows the results of a series of determinations taken over a temperature range 15 to 30.1°. In this case, where the excess gases were expelled, $P_{\text{NH}_3} = P_{\text{H}_2\text{Se}} = P/2$, where P is the observed pressure at equilibrium. The equilibrium constant then becomes, $K_p = (P/2)^2$. The dissociation pressures were found

(1) Presented as a thesis in partial fulfillment of the requirements for the Master of Science degree in chemistry.

(2) Isambert, *Compt. rend.*, **92**, 919 (1881).

(3) Magnusson, *J. Phys. Chem.*, **11**, 21 (1907).

TABLE I
DISSOCIATION OF AMMONIUM HYDROSULFIDE (15 to 30.1°)

Initial buret reading, mm.	Final buret reading, mm.	Temperature, °C.	Pressure, mm. of Hg	$K_p \times 10^4$ (p in atm.) Average
456.8	463.6	15.0	6.8	0.20
510.2	517.0		6.8	
433.5	540.2		6.7	
486.7	494.4	17.0	7.7	.25
434.4	442.0		7.6	
502.9	510.6		7.7	
510.3	518.9	18.0	8.5	.31
472.3	480.9		8.6	
447.7	456.0		8.3	
436.3	445.4	19.0	9.1	.36
481.6	490.6		9.0	
510.5	519.6		9.1	
437.5	447.8	21.0	10.3	.45
475.9	486.1		10.2	
510.9	521.1		10.2	
429.4	441.3	23.0	11.9	0.62
477.8	489.9		12.1	
510.9	522.9		12.0	
405.7	419.8	24.8	14.1	0.85
463.5	477.7		14.1	
514.0	527.9		13.9	
416.1	434.0	27.7	17.9	1.4
470.3	488.5		18.2	
509.1	527.1		18.0	
423.8	444.6	29.3	20.8	1.9
468.3	489.2		20.9	
512.7	533.6		20.9	
441.1	441.1	30.1	23.2	2.3
472.6	495.6		23.0	
510.0	533.0		23.0	

to be independent of the volume when the volume was varied between 10 and 40 ml.

TABLE II
EQUILIBRIUM WITH EXCESS AMMONIA

Excess $\text{NH}_3 = 0.301 \times 10^{-4}$ mole; temp. = 30.0°; bar. P. = 748.1 mm.

Height of leveling bulb, mm.	mercury, mm.		Observed pressure, mm.	Volume, ml.	$K_p \times 10^4$
	Buret				
72.0	778.3		41.8	15.50	1.7
250.0	967.0		31.1	30.10	2.6
257.8	980.0		25.9	50.35	2.4
263.7	987.2		24.6	64.85	2.3
267.1	992.0		23.2	83.10	2.1
268.5	994.0		22.6	92.60	2.1

TABLE III

EQUILIBRIUM WITH EXCESS HYDROGEN SELENIDE

Excess $\text{H}_2\text{Se} + \text{H}_2 = 1.013 \times 10^{-4}$ mole; temp. = 31.5°; bar. P. = 740.0 mm.

Height of leveling bulb, mm.	mercury, mm.		Observed pressure, mm.	Volume, ml.	$K_p \times 10^4$
	Buret				
714.8	37.7		62.9	32.95	2.2
710.1	16.1		46.0	47.30	1.9
705.0	0.8		35.8	68.40	2.0
755.0	46.6		31.6	85.00	2.0
751.8	42.1		30.3	98.07	2.4

Tables II and III show the results obtained using excesses of ammonia and hydrogen selenide, respectively. In the former case the total pressure, P is equal to $P_{\text{H}_2\text{Se}} + p'_{\text{NH}_3} + p''_{\text{NH}_3}$, where p'_{NH_3} is the pressure due to the dissociation of the solid ammonium hydroselenide and p''_{NH_3} is the pressure due to the excess ammonia. Hence the partial pressure of hydrogen selenide, $P_{\text{H}_2\text{Se}}$ is equal to $P - p''_{\text{NH}_3}/2$, and that of ammonia, P_{NH_3} is equal to $p'_{\text{NH}_3} + p''_{\text{NH}_3}$.

The calculations in the case of the excess hydrogen selenide were further complicated by the presence of hydrogen, as a result of the decomposition of the hydrogen selenide into hydrogen and selenium. Here p_{NH_3} is equal to $P - p_{\text{H}_2} - p'_{\text{H}_2\text{Se}}/2$ where $p'_{\text{H}_2\text{Se}}$ is the pressure due to the excess hydrogen selenide. The sample of hydrogen selenide used in obtaining the above data contained 6.6% hydrogen.

The small value of the equilibrium constants and the presence of an excess of one of the gases makes the partial pressure of the second gas very small. A small error in the measurements would cause a large error in calculating this pressure and also in the value of K_p . However, the values of the K_p obtained when excesses were used were of the same order of magnitude as those obtained when the excess gases were expelled.

A plot of $\log K_p$ vs. $1/T$, shown in Fig. 2, gives a straight line, indicating that the data herein presented satisfy the requirements of van't Hoff's equation, $\log K_p = -\Delta H/2.303 \cdot RT + \Delta S/2.303 R$. The slope of the line is $-6,020$,

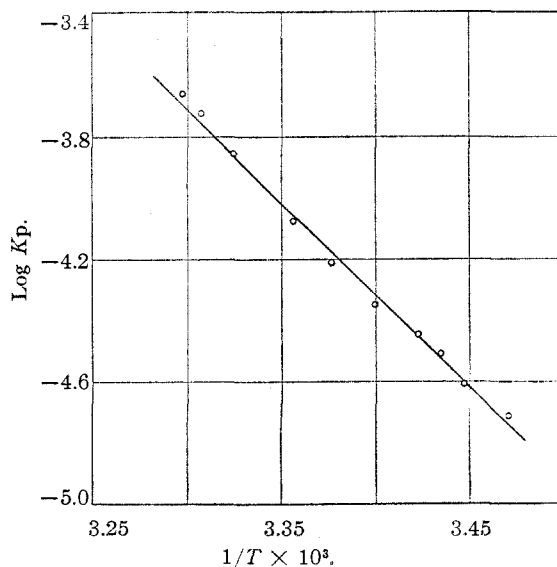


Fig. 2.

hence ΔH for the dissociation is 27,600 calories within the indicated temperature range.

Results of the addition of hydrogen selenide to ammonia at 21°, Table IV, show that the two gases react mole for mole in the formation of

TABLE IV

Ml. of H ₂ Se + H ₂	Ml. of H ₂ Se	Ml. of NH ₃ required
26.6	25.0	25.0
23.4	21.9	22.2
27.7	25.9	25.8
22.4	20.9	21.1

the white crystalline solid. Therefore, the product must be NH₄HSe.

Summary

1. The equilibrium for the dissociation of ammonia hydroselenide, NH₄HSe(s) \rightleftharpoons NH₃(g) + H₂Se(g), was determined in the temperature range 15° to 30.1°.

2. ΔH for this reaction was found to be 27,600 calories in the indicated temperature range.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Rotation in the Solid Forms of Some Long-Chain Alcohols¹

BY JOHN D. HOFFMAN AND CHARLES P. SMYTH

X-Ray investigations on *n*-dodecyl alcohol conducted by Bernal^{1a} resulted in the conclusion that the molecules rotate about their long axes several degrees below the freezing point. This result is not in accord with the more recent X-ray measurements of Ott² who found no evidence for rotation. Dielectric data on this substance obtained by Frosch³ at audio frequencies disclosed strong frequency dispersion below the freezing point which would require molecular rotation in the solid if interpreted in the usual way, but the results showed great complexity and were not reproducible.

Dielectric measurements⁴ on *n*-hexadecyl alcohol carried out at 0.5, 5.0 and 50 kc. indicated molecular rotation in a definite temperature range below the freezing point. It is noted that the dielectric loss factor, ϵ'' , in this range, which we term the "waxy" range to avoid the term "glassy," greatly exceeded the theoretical limit for orientation loss imposed on it by the relation $\epsilon''_{\max} = (\epsilon_0 - \epsilon_\infty)/2$. Furthermore, the dielectric constant ϵ' rose sharply on freezing and was frequency dependent. The rise in dielectric constant would seem to demand greater molecular freedom in the solid than in the liquid, which is contrary to the fact that entropy must decrease on freezing. It must be pointed out, however, that X-ray observations² on *n*-hexadecyl alcohol showed that hexagonal close-packing of the molecular chains persisted for some degrees below the freezing point, which strongly suggests molecular rotation in the solid. Frosch explained the high value of the dielectric constant mentioned above as due to the co-existence of liquid and solid phases between the condenser plates, which resulted in Maxwell-Wagner polarization. The persistence of the

liquid phase in contact with the solid for a long period of time at a temperature several degrees below the freezing point appears highly improbable, although a treatment based on this model accounted quantitatively for the observed dielectric constants.

The present work undertakes the study of the reported transition in *n*-dodecyl alcohol, and the investigation of the dielectric and thermal behavior of *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohols with emphasis on the status of molecular rotation about the long axis and the isolation of the factors leading to time and frequency dependence of the abnormally high dielectric constants.

Experimental Method

The bridge employed for the measurements was essentially that described in previous papers.⁵ The frequency range and stability of the equipment were improved by using a Hewlett-Packard 200 oscillator as a signal generator and a TS12/AP amplifier (Presto Recording Corp.) as a null detector. Teflon spacers were inserted between the gold cylinders of the dielectric cell ($C_0 = 38.6 \mu\mu\text{f}$; liquid capacity, 8 cc.) instead of the customary mica tabs with the result that loss across the tabs was eliminated. All temperature measurements were made with a calibrated platinum resistance thermometer.

The dielectric constants were determined by calculating the ratio, $\epsilon' = C/C_0$, where C is the capacitance of the cell containing the material, exclusive of lead and insulator capacitance, and C_0 is the corresponding vacuum capacitance. The specific conductivity in ohms⁻¹ cm.⁻¹ was calculated from the relation $k = 0.0885/RC_0$ where R is the resistance of the cell in ohms as measured in the bridge, C_0 being expressed in $\mu\mu\text{f}$. ϵ'' was calculated from k by using the relation $\epsilon'' = 1.8 \times 10^{12} k/f$, where f is the frequency of the measurements in cycles/sec. The error in ϵ' never exceeds $\pm 1\%$, and the reproducibility in the ϵ'' measurements is better than $\pm 3\%$ except for very low values where the error becomes greater.

Purification of Materials

n-Dodecyl alcohol (C₁₂H₂₆OH) was purified by crystallization from dry ether followed by five fractional distillations at 1 mm., f.p. 23.5°. Beilstein (I-432) gives the f.p. as 24°.

(1) This research was carried out with the support of the Office of Naval Research.

(1a) Bernal, *Nature*, **129**, 870 (1932).

(2) Ott, *Z. physik. Chem.*, **193**, 218 (1944).

(3) Frosch, *Ann. Physik*, **42**, 254 (1942).

(4) Baker and Smyth, *This Journal*, **60**, 122 (1938).

(5) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); *ibid.*, **55**, 1830 (1935).