

PROPERTIES:

Water-clear liquid. B.p. 37°C , m.p. -80°C . Very mobile and extremely explosive. However, even concentrated solutions can be handled without too much danger. Unbearably pungent odor. Inhalation of the vapor causes dizziness, headache and strong irritation of the mucous membranes.

REFERENCES:

- L. M. Dennis and H. Isham, J. Amer. Chem. Soc. 29, 27 (1907).
P. Günther and R. Meyer, Z. Elektrochem. 41, 541 (1935).
J. Einig, German Patent 435 654, from Chem. Zentr. 1926 II, 3072.
W. Hoth and G. Pyl, Angew. Chem. 42, 888 (1929).
A. W. Browne, J. Amer. Chem. Soc. 27, 551 (1905).
J. Martin, J. Amer. Chem. Soc. 49, 2133 (1927).
L. F. Audrieth, Chem. Rev. 15, 169 (1934).

SOLUTIONS OF HYDRAZOIC ACID

Because of the very high danger of explosion with pure HN_3 , it is expedient to work only with its relatively harmless solutions.

I. Aqueous solution: A solution of NaN_3 (15 g.) and NaOH (5 g.) is prepared in 150 ml. of water in a 250-ml. distillation flask equipped with an addition funnel and a high-efficiency condenser. The end of the condenser is connected by means of an adapter to a 500-ml. suction flask, which contains 100 ml. of water. The suction outlet of the flask is connected to a tube leading directly to the hood. The contents of the flask are heated to boiling (very important!), and 90 ml. of 40% H_2SO_4 is added dropwise. The distillation is continued until about 50 ml. of the solution remains in the flask. In this manner one obtains a solution containing about 3% HN_3 (0.6-0.7N). The initial addition of NaOH is a precautionary measure which definitely precludes too high a concentration of HN_3 in the cold solution.

II. *Anhydrous Ether Solution*: Since the distribution of HN_3 between water and ether is approximately 1 : 7, one can extract an aqueous solution of HN_3 with ether. However, even in this case it is preferable to use a distillation method: NaN_3 (30 g.) is dissolved in 100 ml. of water, 150 ml. of ether is added, and the mixture is placed in a 500-ml., round-bottom flask. The latter is equipped with an adapter fitted to a condenser, followed by a suitable ice-cooled receiver flask containing 100 ml. of ether. The round-bottom flask is also equipped with an addition funnel, the tip of which is immersed in the liquid and through which 30 ml. of concentrated H_2SO_4 is slowly added. The bulk of the ether and HN_3 distill off during the addition of the H_2SO_4 . The remainder

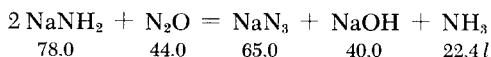
is driven off by heating on a steam bath. The ether distillate is dried over CaCl_2 and then distilled from this desiccant.

REFERENCES:

- W. S. Frost, J. C. Cothran and A. W. Browne, *J. Amer. Chem. Soc.* **55**, 3516 (1933).
 L. F. Audrieth and C. F. Gibbs in: H. S. Booth, *Inorg. Syntheses*, Vol. I, New York-London 1939, p. 77.

Azides

SODIUM AZIDE, NaN_3



Sodium azide is prepared in the same apparatus used for the preparation of sodium amide (see Fig. 177, p. 459). Following the preparation of sodium amide, an N_2O generator (from ammonium nitrate) is attached instead of the ammonia generator (see Fig. 179, p. 470). The N_2O outlet tube is equipped with a glass tee immersed in mercury. It acts as a pressure release valve should the inlet tube plug. The water, formed together with the N_2O , is collected in the receiver (Fig. 184). Finally, the gas is well dried over soda lime and sodium hydroxide before reaching the reactor (Fig. 177). The N_2O inlet tube may not dip into the sodium azide melt since NaN_3 is solid at the reaction temperature and thus would plug the tube. About five hours are required for the conversion of 25 g. of NaNH_2 to NaN_3 . The crude product obtained must be recrystallized from water unless it is used for the preparation of HN_3 or other azides.

Other methods of preparation: $\text{N}_2\text{H}_4 + \text{HNO}_2 = \text{HN}_3 + 2\text{H}_2\text{O}$. Hydrazine hydrate (5 g.) is dissolved in 50 ml. of absolute ether, the solution cooled with ice, and 37.5 ml. of 4N sodium methoxide solution and 12.6 ml. of ethyl nitrite are added. The solution is allowed to stand for a while in the ice and is then slowly warmed to room temperature. The NaN_3 precipitates and is washed, after suction filtration, with a methanol-ether mixture. If hydrazine hydrate is unavailable, the corresponding quantity of hydrazine sulfate can be used. It is ground with the methoxide solution, and the sodium sulfate precipitated is filtered off. After the addition of ether, the solution so obtained is reacted with ethyl nitrite. One then proceeds as described above.

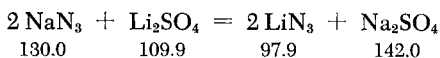
Another procedure is to dissolve 26 g. of hydrazine sulfate in 140 ml. of sodium hydroxide solution (containing 28 g. of NaOH),

add 22 ml. of ethyl nitrite, and shake the mixture for six hours in a pressure bottle. The unreacted ethyl nitrite is purged with air, and the alcohol is similarly removed on a water bath. The solution is used directly for the preparation of HN_3 .

For the procedure for the preparation of N^{15} -labeled NaN_3 , see p. 466.

REFERENCES:

- L. M. Dennis and A. W. Browne, *Z. anorg. allg. Chem.* **40**, 95 (1904).
 W. Wislicenus, *Ber. dtsch. chem. Ges.* **25**, 2084 (1892).
 K. Clusius and E. Effenberger, *Helv. Chim. Acta* **38**, 1834 (1955).

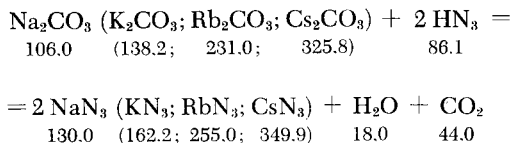
LITHIUM AZIDE, LiN_3 

With gentle warming, NaN_3 (91.30 g.) and $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ (1.41 g.) are dissolved in 7 ml. of H_2O . Then 35 ml. of 96% alcohol is added with shaking. The solution is filtered after ten minutes and the residue of Na_2SO_4 and LiSO_4 washed with alcohol. The filtrate and wash solutions are evaporated on a water bath and dried in a drying oven at 80°C . This crude product is digested at 35°C for two minutes with 10 ml. of 96% alcohol and filtered, and the solution is dried as described above. The yield is 0.6 g of 99.5% LiN_3 .

REFERENCE:

- N. Hofmann-Bang, *Act. Chem. Scand.* **11**, 581 (1957).

ALKALI AZIDES FROM CARBONATES



According to Suhrmann and Clusius, the required quantity of HN_3 is prepared in the following manner. The NaN_3 and the calculated amount of 6% H_2SO_4 are placed in a 300-ml., round-bottom Pyrex flask equipped with a ground glass stopper. A distillation tube, sufficiently long to prevent spraying over, is fused laterally to the neck of the flask. The tube end is immersed in a Pt dish filled with an alkali carbonate solution (for the preparation of pure alkali carbonates see p. 987) so that the HN_3 which

comes over is completely absorbed. In order to ensure complete conversion of the carbonate to the azide, an excess of HN_3 is used. After the reaction is complete, the alkali azide solution is evaporated on a water bath until the onset of crystallization. Crystallization on cooling is carried out without disturbing the solution to prevent the inclusion of mother liquor. After standing for several hours, the crystalline paste is separated from the mother liquor by suction filtration in a Pt Gooch crucible and washed with small quantities of distilled water. The crystals are dried in a drying oven at about 80°C and stored in a desiccator over P_2O_5 . The stoppers of the flask and the lid of the desiccator are not greased in order to avoid contamination of the preparation.

PROPERTIES:

NaN_3 : Formula weight 65.02. Decomposes at 275°C without melting. Solubility (17°C) 41.7 g./100 g. H_2O ; (16°C) 0.315 g./100 g. absolute alcohol; insoluble in ether. $d(x\text{ ray})$ 1.838. F5_1 structure type.

KN_3 : Formula weight 81.12. M.p. 343°C , decomp. t. 355°C . Solubility (water) (0°C) 41.1 g., (17°C) 49.6 g., (100°C) 105.7 g./100 g. H_2O ; (alcohol, 16°C) 0.137 g./100 g. absolute alcohol; insoluble in ether. $d(x\text{ ray})$ 2.045. F5_2 structure type.

RbN_3 : Formula weight 127.50. M.p. 321°C , decomp. t. 395°C (in a quartz tube). Solubility (16°C) 107.1 g./100 g. H_2O ; 0.182 g./100 g. absolute alcohol; insoluble in ether. d 2.788. Probably F5_2 structure type.

CsN_3 : Formula weight 174.93. M.p. 326°C , decomp. t. 390°C (in a quartz tube). Solubility (16°C) 307.4 g./100 g. H_2O ; 1.037 g./100 g. absolute alcohol; insoluble in ether.

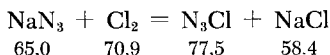
REFERENCE:

R. Suhrmann and K. Clusius, *Z. anorg. allg. Chem.* 152, 52 (1926).

Azides of Be, Mg, B, Al, Ga, Si: Their preparation is described by E. Wiberg and H. Michaud, *Z. Naturforschg.* 9 b, 495 (1954); see also section on Alkaline Earth Metals.

Chlorine Azide

ClN_3



I. A solution of chlorine azide in CCl_4 is prepared by mixing a solution of NaN_3 in water with a solution of NaOCl . The reaction follows the above equation. A layer of CCl_4 is introduced underneath the NaOCl and the mixture is acidified with boric or acetic