

Fig. 185. Preparation of nitrogen dioxide. *r*) Tube of high melting glass; *a* and *b*) seal-off points; 1) mercury valve; 2) concentrated  $H_2SO_4$ ; 3, 4) soda lime; 5) ice-salt-cooled trap; 6)  $PbO_2$ ; 7)  $P_2O_5$ ; 8, 9) condensation traps; 10) storage ampoules; 11) drying agent.

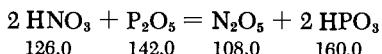
#### PROPERTIES:

Formula weight 46.01. Brown, extremely poisonous gas. Absorbed by alkali, forming nitrite and nitrate. M.p.  $-10.8^{\circ}C$ , b.p.  $21.2^{\circ}C$ .

#### REFERENCES:

- M. Bodenstein, Z. phys. Chem. 100, 68 (1922).
- A. Klemenc and J. Rupp, Z. anorg. allg. Chem. 194, 51 (1930).
- P. A. Guye and G. J. Druginin, J. Chim. Phys. 8, 489 (1910).
- F. E. C. Scheffer and C. P. Treub, Z. phys. Chem. 81, 308 (1913).
- A. Klemenc, Die Behandlung und Reindarstellung von Gasen [Treatment and Purification of Gases], Vienna, 1948, p. 207.

### Nitrogen Pentoxide



Nitric acid, as concentrated as possible ( $d\ 1.525$ ), is cooled with an ice-salt freezing mixture and carefully dehydrated with excess  $P_2O_5$ , using adequate cooling and small batches of acid. The mixture is then distilled very slowly from a retort — preferably in a stream of oxygen containing some ozone. The apparatus must not contain any stoppers or connections made of organic material. The yield is about 80 g. of  $N_2O_5$  from 150 g. of  $HNO_3$ .

Cäsar and Goldfrank recommend freezing 70–80 ml. of highly concentrated  $HNO_3$  ( $d\ 1.5$ ) contained in a large, three-neck, round-bottom flask cooled with Dry Ice mixture (see Fig. 186). An  $O_2$  stream containing ozone is passed through the flask and

100-125 g. of  $P_2O_5$  is added at once through the central tube. The tube is closed immediately with a glass stopper. The mixture is then allowed to thaw slowly. A room temperature water bath may be used to accomplish this. Large quantities of  $N_2O_5$  mixed with  $N_2O_4$  are rapidly evolved and are condensed in the large trap *b*, which is cooled to  $-78^{\circ}C$ . When most of the product (recognizable by its reddish vapors) has been transferred, the flask is shaken, and when the renewed evolution of gas again decreases, the flask is heated for several hours in a stream of  $O_2$  containing  $O_3$ . When all the product gas has been transferred and condensed, the trap is removed and the condensate fractionated by vacuum distillation.

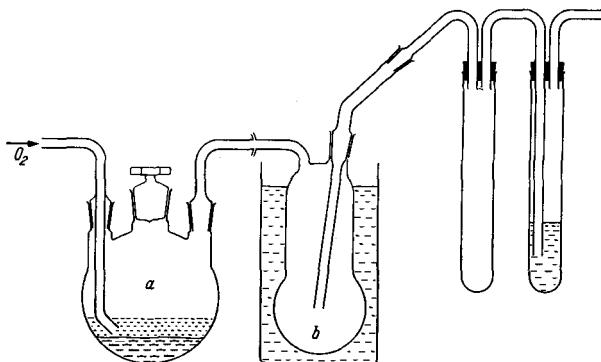


Fig. 186. Preparation of nitrogen pentoxide. *a*) Three-neck round-bottom flask with a ground glass stopper; *b*) condensation trap with Dry Ice bath.

*Other preparative methods:* From  $AgNO_3$  and  $Cl_2$  or from  $AgNO_3$  and  $POCl_3$ . It is best to introduce ozone-containing oxygen into the liquid  $N_2O_4$ . For example, 5 g. of liquid  $N_2O_4$  is placed in a U tube cooled in an ice-salt mixture. Oxygen containing 6-7% ozone is passed through the tube for one hour.

#### PROPERTIES:

Colorless crystals which decompose slowly at room temperature and are moderately stable only below  $10^{\circ}C$ . The melting point has not been determined. Subl. t.  $34^{\circ}C$ . According to R. Schwartz,  $N_2O_5$  reacts with  $H_2O_2$  with the formation of pernitric acid:  $N_2O_5 + H_2O_2 = HNO_4 + HNO_3$ .

#### REFERENCES:

W. Biltz, W. Fischer and E. Wünnenberg, Z. anorg. allg. Chem. 193, 360 (1930).

- H. J. Schumacher and G. Sprenger, Z. phys. Chem. A 140, 274, 277 (1929).  
 F. Russ and E. Pokorny, Mh. Chem. 34, 1051 (1913).  
 R. Schwarz, Z. anorg. allg. Chem. 256, 3 (1947); see also L. Hack-spill and J. Besson, Bull. Soc. Chim. France, Mém. (5) 16, 479 (1949).  
 G. V. Caesar and M. Goldfrank, J. Amer. Chem. Soc. 68, 372 (1946).  
 N. S. Gruenhut, M. Goldfrank, M. L. Cushing and G. V. Caesar, in L. F. Audrieth, Inorganic Syntheses, Vol. III, New York-Toronto-London 1950, p. 78.

### Nitric Acid



When necessary, purification of technical-grade nitric acid in the laboratory is accomplished by distillation over a small amount of  $\text{AgNO}_3$ . The first and last fractions are discarded; the resulting acid is free of halogens.

Several methods have been suggested for the preparation of anhydrous nitric acid.

I. Acid of the highest possible concentration is distilled; then an inert, dust-free gas stream, preferably preheated, is passed through to remove the nitrogen oxides. It is ultimately distilled over  $\text{P}_2\text{O}_5$ . Analysis then indicates whether the acid contains free  $\text{N}_2\text{O}_5$ . If so, some dilute acid, containing enough water to dissolve the  $\text{N}_2\text{O}_5$  present, is added.

II. By distillation with  $\text{H}_2\text{SO}_4$ . The starting material is acid of the highest possible concentration; the apparatus shown in Fig. 187 is used. A 600-ml. glass flask is equipped with a ground glass joint with a boiling capillary *a* and a ground glass thermometer *b*. An efficient condenser is attached at *c* and terminates in a receiver. The apparatus is connected to an aspirator via a safety trap. The three-way stopcock also permits attaching a manometer. The distillation flask is filled with 150 ml. of  $\text{HNO}_3$ , 300 ml. of  $\text{H}_2\text{SO}_4$ ,

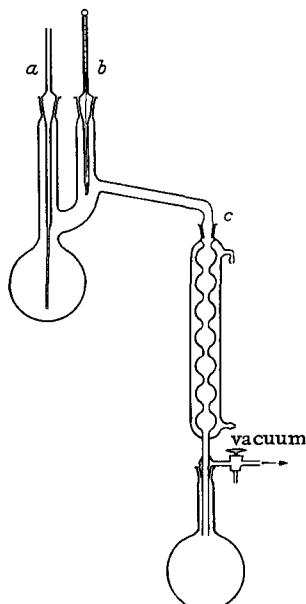


Fig. 187. Preparation of anhydrous nitric acid.

both precooled in an ice-salt mixture. Cooling should be continued during the mixing process. The apparatus is then evacuated and carefully heated on a water bath. Colorless HNO<sub>3</sub> passes into the receiving vessel at 22 mm. and 37-40°C. The condensate is redistilled in the same manner, using twice the volume of concentrated H<sub>2</sub>SO<sub>4</sub>. At 20 mm. the pure acid distills over between 36 and 38°C. The ground glass joints should obviously not be lubricated with any organic material. If a sealing agent is necessary, some P<sub>2</sub>O<sub>5</sub> or H<sub>2</sub>SO<sub>4</sub> may be used.

It is also recommended that a stream of oxygen containing some ozone be passed through the highly concentrated acid and that it be distilled under aspirator vacuum.

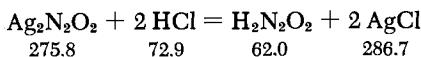
#### PROPERTIES:

Formula weight 63.02. B.p. 83°C (increases after some boiling to 87°C because of decomposition), m.p.—41°C. After dilution with twice the amount of water, nitric acid not containing nitrogen oxides does not discolor KMnO<sub>4</sub>. d<sub>4</sub><sup>15</sup> 1.522. Pure, 100% acid cannot be kept without decomposition for a very long time, especially in the light. Aqueous HNO<sub>3</sub> has a boiling point maximum at 121°C (68% HNO<sub>3</sub>).

#### REFERENCES:

- J. Giersbach and A. Kessler, Z. phys. Chem. 2, 690 (1888).
- L. Meyer, Ber. dtsh. chem. Ges. 22, 23 (1899).
- V. H. Voley and J. J. Manley, Proc. Roy. Soc. London 62, 223 (1897); 68, 128 (1901).
- R. Lüdemann, Z. phys. Chem. B 29, 136 (1935).
- E. Briner, B. Susz and P. Favarger, Helv. Chim. Acta 18, 376 (1935).
- A. Klemenc and E. Ekl, Mh. Chem. 39, 641 (1918).
- A. Potier, Comptes Rendus Hebd. Séances Acad. Sci. 233, 1113 (1951).

### Hyponitrous Acid



Ether, dehydrated over Na wire, is saturated with dry HCl, cooled and treated with Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub> until the yellow color of the latter persists. Complete exclusion of atmospheric moisture is required. The solution is rapidly filtered through a dry filter