Demonstration experiments

to the presentation

"Teaching Thermodynamics: Chemical Potential from the Beginning"

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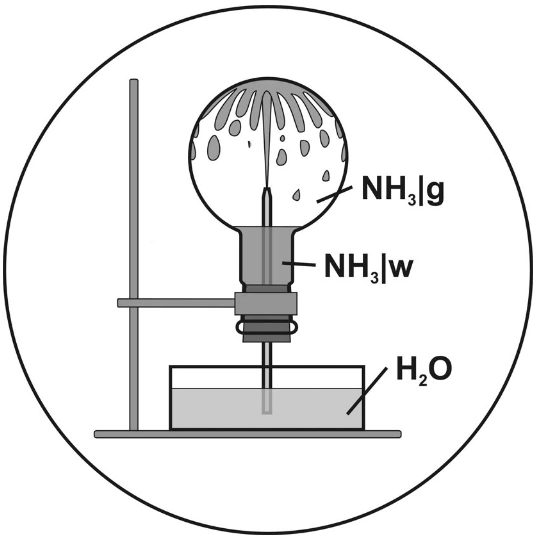
Ammonia Fountain



Equipment:

2-L round-bottomed flask
dropping funnel
250-mL round-bottomed flask with two necks
for dropping funnel and glas tube
glass tubes (diameter: 7-8 mm)
flexible tube
ring stands, clamps and ring
glass tube with tapered end
  (length: approx. 30 cm, diameter: 7-8 mm)
rubber stoppers with one and two holes
small rubber stopper
crystallization dish or beaker
blow-dryer

Chemicals:

concentrated ammonia solution
sodium hydroxide pellets
distilled water
phenolphthalein solution
dilute hydrochloric acid

Safety:

ammonia solution (NH_3): C, N R34-50 S26-36/37/39-45-61
sodium hydroxide (NaOH): C R35 S26-37/39-45
phenolphthalein solution ($C_{12}H_{14}O_4$) (in ethanol): R10

 C  N

Ammonia is a colourless, highly corrosive and irritant gas which is especially harmful to the respiratory system and the eyes. Therefore, the round-bottom flask has to be filled in a fume hood. It is also necessary to wear safety glasses and protective gloves.

To avoid implosion-related incidents caused by the stress of the vacuum created during the experiment damaged glassware (with “stars”, cracks etc.) never should be used.

Procedure:

Preparation: A relatively dry sample of ammonia gas can be prepared by dropping concentrated ammonia solution onto granular sodium hydroxide. Therefore, 15 g of NaOH pellets are put into the 250-mL round-bottomed flask. The dropping funnel is attached to the flask and the second neck is closed by a rubber stopper with one hole combined with a glass tube. The flask is connected by a flexible tube to the 2-L round bottom flask which was closed by a rubber stopper with two holes and a L-shaped glass tube and mounted upside down to a stand. 30 mL concentrated ammonia solution are filled into the dropping

funnel and dripped into the 250-mL flask. The developed dry gas fills the 2L-flask by downward displacement of air. After the reaction the flask is sealed with a stopper and the glass tube with the tapered end inside and about half of the way up the bulb of the flask. The flask is heated by a blow-dryer and subsequently the end of the glass tube is sealed with a small rubber stopper.
Procedure: The crystallization dish is filled with distilled water and the indicator phenolphthalein as well as a few drops of hydrochloric acid are added. The inverted 2L-flask is clamped on the stand over the crystallization dish so that the bottom end of the glass tube is immersed deeply in the water and secured by a ring. Then the small rubber stopper is removed.

Observation:

The water begins to go up in the glass tube because of slight underpressure. When the first drops reaches the bulb the speed of the process increases more and more till the water shoots into the glass flask like a fountain. Additionally, the solution turns pink. The water level rises until the flask is nearly completely filled.

Explanation:

Ammonia gas is extremely soluble in water (1 L water can dissolve 702 L ammonia gas at 20 °C!). The fountain experiment demonstrates this violence with which ammonia is absorbed by water. The process can be explained thermodynamically by use of the chemical potential:

$$NH_3|g \rightarrow NH_3|w$$

$$\mu^{\ominus}: \quad -16{,}4 \; > \; -26{,}4 \quad kG$$

⇨ chemical drive: + 10,0 kG

The drive of the reaction is positive, i.e. the reaction takes place spontaneously.

The first few water drops that enter the round-bottomed flask dissolve part of the ammonia gas thereby reducing its volume considerably. This causes a decrease in pressure in the flask and more water is drawn from the reservoir into the bulb. As more and more water rushes into the flask, more and more of the ammonia gas dissolves creating a larger pressure difference, thereby speeding up the flow of the water.

The aqueous ammonia solution is a weak base because of the protolysis reaction:

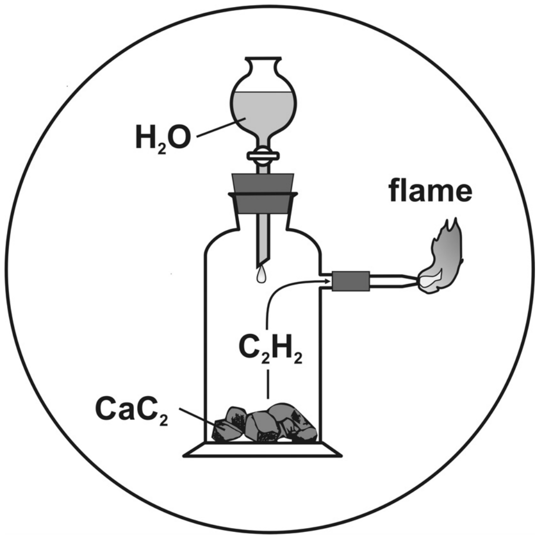
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- .$$

This alkaline effect of ammonia is demonstrated by addition of the indicator phenolphthalein which changes its colour to pink.

Disposal:

The solution is neutralized with hydrochloric acid and poured down the drain.

Carbide Lamp



Equipment:

washing bottle with dropping funnel
rubber tubing
glass tube with tapered end
matches or pocket lighter
wooden splint
test tube

Chemicals:

calcium carbide (ideal grain size: 20 – 40 mm)
destilled water

Safety:

calcium carbid (CaC_2): F R15 S8-43.6
ethyne (acetylene) (C_2H_2): F+ R5-6-12 S9-16-33
calcium hydroxide ($Ca(OH)_2$: Xi R41 S(22-)24-26-39

 F(+)  Xi

Ethyne is extemely flammable and forms explosive mixtures with air ("detonating gas"). Because the gas is poisonous particularly with regard to contaminants it is necessary to work in a fume hood. It is also required to wear safety glasses.

Procedure:

The dropping funnel is filled with water and some lumps of calcium carbide are placed in the washing bottle. Water is dripped **cautiously!** onto the calcium carbide until a vigorous generation of gas begins. Then the cock of the dropping funnel is closed and the escaping gas is collected in the test tube. The existence of an explosive mixture can be tested by ignition with a burning splint. When the explosion danger is overcome, i.e. most of the air in the washing bottle is displaced by ethyne, the gas can be ignited directly at the tapered end of the glas tube by the splint (eventually it is necessary to drip again some water onto the carbide). For avoiding any explosion danger it is recommended to fill the washing bottle with nitrogen before starting the experiment.

Observation:

The produced gaseous ethyne burns with a bright and sooty flame. Additionally, an unpleasant garlic-like ordour can be noticed.

Explanation:

Calcium carbide reacts with water under formation of ethyne (acetylene) according to

$$\frac{CaC_2|s + 2\ H_2O|l \rightarrow Ca(OH)_2|w + C_2H_2|g}{}$$

$\Sigma\mu^{\ominus}$: -542,2 > -658,4 kG

⇒ chemical drive $\mathcal{A}$: + 116,2 kG

The drive of the reaction is positive, i.e. the reactants combined have a higher chemical potential than the products and subsequently the reaction takes place spontaneously.

Necessary chemical potentials (T = 298 K, p = 101,3 kPa):

Substance	Chemical potential $\mu^{\ominus}$ [kG]
CaC_2|s	-67,8
H_2O|l	-237,2
Ca^{2+}|w	-553,0
OH^-|w	-157,3
C_2H_2|g	+209,2

Therefore, a positive chemical potential like in the case of ethyne does not mean that the substance can not be produced by normal reactions of stable substances (with negative μ) but only that it tends to decompose into its elements (however, this process can possibly proceed very slowly like in the case of benzene).

The “burning test” demonstrates that the produced ethyne reacts with oxgen in the air describable by

$$2\ C_2H_2|g + 5\ O_2|g \rightarrow 4\ CO_2|g + H_2O|l.$$

In earlier times, the gas extracted from the above reaction was used to power miners’ lamps and bicycle lights because of its bright flame. It is still used today for welding because of its high combustion temperature.

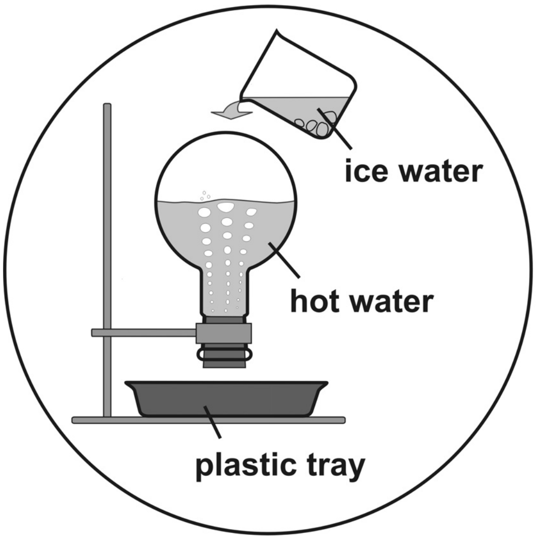
The characteristic “carbide ordour”, however, is not caused by ethyne but by the toxic gas phospine released by the contaminant calcium phosphide on contact with water.

Pure calcium carbide forms colourless, transparent crystals. Mostly the technical product is commercially available which is composed of greyish black or brown lumps. The colour is caused by contamination with carbon and iron oxide. Other contaminants are calcium oxide, calcium phosphide mentioned above, calcium sulfide, calcium nitride and silicium carbide.

Disposal:

After the burning of the produced ethyne the residue should completely react with water in the fume hood. The produced solution of calcium hydroxide is neutralised and flushed down the drain with water.

Boiling by Cooling



Equipment:

1-L round-bottomed flask
heating mantle or burner with wire gauze
rubber stopper
beaker
plastic tray
ring stand, clamp

Chemicals:

water
crushed ice

Safety:

To avoid implosion-related incidents caused by the stress of the vacuum created during the experiment damaged glassware (with "stars", cracks etc.) never should be used. It is also necessary to wear always safety glasses.

Procedure:

The round-bottomed flask is filled to one half with water and a few boiling stones are added. The water is heated until boiling by a heating mantle or burner and allowed to boil for a few minutes so that most of the air is driven out of the flask. The flask is removed from the heat, tightly stoppered and allowed to cool for a little while to make a good seal. Then the inverted flask is clamped on the stand over a plastic tray, secured by a ring and ice water is poured cautiously over the flask.

Observation:

The water inside the flask begins to boil heavily. When the pouring is stopped also the boiling process comes to an end after a little while. But the boiling starts up again by use of more ice water. The whole "procedure" can be repeated several times.

Erklärung:

The boiling process can be described by the following equation:

$$H_2O|l \rightarrow H_2O|g$$

Liquid water has a smaller chemical potential than water vapour under standard conditions (298 K, 101 kPa), i.e. the drive is negative and the process will not take place.

Substance	Chemical potenzial $\mu^{\ominus}$ [kG]	pressure coefficient β [G/Pa]
$H_2O|l$	-237,2	$18{,}1 \cdot 10^{-6}$
$H_2O|g$	-228,6	$24465 \cdot 10^{-6}$

But the chemical potential of gases and therefore also that of water vapour is strongly pressure dependent shown by a high pressure coefficient. At sufficiently low pressure the chemical potential of water vapour will fall below the value of liquid water so that the water boils at temperatures significantly less than 100°C.

The flask is completely filled with water, i.e. liquid water in equilibrium with water vapour. The cooling of its upper part causes the water vapour to condense and the pressure of the vapour drops quickly to a low value.