II—A second sample was diluted with 5 times its weight of water.

Brix of diluted molasses by pycnometer at 26.2° C. = 15.51.

Brix corrected = 15.42.

Brix original = $6 \times 15.42 = 92.52$.

500 cc. of this diluted molasses were clarified with 30 g. dry lead and gave, when analyzed, the following results:

Direct reading (400 mm. tube) = 35.53.

Invert reading (26.3° C.) = -15.17.

Clerget reading = 39.32.

Sucrose (from tables) = 9.66.

Sucrose in original molasses = $9.66 \times 6 \times \frac{1}{3} \times \frac{200}{400} = 38.64$ per cent.

Gravity purity = 41.73.

SUMMARY

In an attempt to explain the discrepancies in results obtained in Clerget sucrose determinations in waste molasses, a large amount of experimental evidence indicates that the method of clarification with lead subacetate solution as recommended by the Hawaiian Chemists' Association yields results from 0.5 to 0.7 per cent too high, this being mostly due to the large volume occupied by the lead precipitate. Clarification with dry lead subacetate gives figures more nearly approaching the true sucrose content of the molasses, but is apt to run a little low, especially if an excess of lead is used in clarifying. A modification of the dry lead method to overcome the dilution error is suggested, and experimental proof of its correctness is offered.

COLLEGE OF HAWAII
DEPARTMENT OF SUGAR TECHNOLOGY
HONOLULU, HAWAII

RELATION BETWEEN EFFICIENCY OF REFRIGERATING PLANTS AND THE PURITY OF THEIR AMMONIA CHARGE¹

By F. W. FRERICHS

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Since writing this paper several months ago a singular case of unpreparedness has developed in the ammonia trade.

As you all know, most ammonia is obtained as a by-product from gas works and from coke oven plants. In gas works and in the older coke oven plants the ammonia is obtained by scrubbing the gas with water and recovering the ammonia from the diluted gas liquor by distillation, whereby free ammonia is obtained, which may be used in the manufacture of aqua and anhydrous ammonia and ammonium salts.

In the more modern coke oven plants the so-called direct process is employed in which only so much ammonia is obtained in the form of ammoniacal liquor as condenses with the water distilling from the carbonized coal. This amounts to only about 20 per cent of the total ammonia. The remaining 80 per cent is obtained by washing the gas with a slightly acid solution of sulfate of ammonium in small apparatus. These plants produce therefore a large amount of sulfate of ammonium, and they are not provided with scrubbers by the use of which all ammonia might be obtained as ammoniacal liquor. This was desirable in peace times because the larger part of ammonium salts was used in the fertilizer trade in the form of sulfate of ammonium.

But when the war demanded ever-increasing quantities of nitrate of ammonium for explosives, the am-

moniacal liquors were insufficient in quantity; and although much sulfate of ammonium was available, there was only one plant in the United States in which aqua ammonia could be made from sulfate, and this plant was entirely engaged in the manufacture of ammonia for the refrigerating industry. And it had become necessary to reconstruct this one plant to adapt it to the use of crude ammoniacal liquor on account of the high price demanded by sulfate of ammonium during the war. Upon request of the Food Administration of the United States, remodeling of the plant was temporarily abandoned and even a 50 per cent increase in capacity of the sulfate plant was agreed to for the purpose of securing ample supply for cold storage warehouses and ice plants, the Government aiding in obtaining a supply of sulfate of ammonium at reasonable cost.

After this was arranged there arose a sudden and large demand for ammonia for the manufacture of nitrate of ammonium, and sulfate of ammonium being the only available material, it had to be manufactured from this ammonium salt.

There exists the singular condition that we have coking plants which are prepared to make much sulfate, but which can make only a limited amount of ammoniacal liquor; and we have nitrate of ammonium plants which can work ammoniacal liquor, but which cannot make nitrate of ammonium from sulfate. We have ample ammonia material, but we are utterly unprepared to make nitrate of ammonium from it.

It is known that in England nitrate of ammonium is made by double decomposition of sulfate of ammonium and nitrate of sodium, but it is understood that in this process about 20 per cent of the ammonia is wasted. To investigate this process a Commission went to England several weeks ago, and their report by cable is expected now. But even in the case of a favorable report, it is estimated that it will require six months before works of sufficient size can be put into operation.

Being familiar with the manufacture of ammonia from sulfate, I was called to Washington to consult with officials of the War Department. Complete plans, patterns, assistance, and patent rights were promptly offered and accepted for the purpose of erecting new plants, each the size of our St. Louis plant, a number of which are contemplated for the various explosive works. We have the singular opportunity of witnessing unprecedented growth of an industry which (economically speaking) has outlived its usefulness, and which after the war must die out, being unprofitable under peace conditions.

Reconstruction of our St. Louis plant is being carried on under great difficulties and I must ask your indulgence if I show you this afternoon a sadly disarranged plant, which must be operated while it is being reconstructed. I had hoped to have the plant finished for this convention, but Government demands changed the plans, and if I wish to keep my promise to you I must show the works as they are now.

The scarcity of ammonia is unprecedented and the importance of saving ammonia has become para-

¹ Paper read at the 10th Annual Meeting of the American Institute of Chemical Engineers, St. Louis, Mo., December 5-8, 1917.

mount. Waste of ammonia must be prevented at almost any cost, so much so that officials of the Government contemplate closing ice plants where waste is permitted to continue.

For these reasons a report of the relation between the efficiency of refrigerating plants and the purity of their ammonia charge is of greatest interest at this time, since it tends to prove that pure ammonia and smallest waste of it are inseparable factors in the operation of refrigerating plants.

When I visited the Loan collection of scientific apparatus exhibited in Kensington Museum, London, England, in 1876, I saw for the first time ice machines on exhibit. They were small affairs, operated with ether, carbon dioxide, sulfur dioxide, or with ammonia by the absorption process.

In the years immediately following, Linde published his classical investigations on the Ammonia Compression Ice Machine, laying thereby the foundation for that type of refrigerating plants, which at present is predominant here and abroad.

In 1880, when I arrived in the United States, artificial refrigeration was still in its infancy. But even at that time the superiority of ammonia as a refrigerating agent for larger plants, in preference to other agents, was well established.

Liquefied ammonia gas, however, had not yet become an article of commerce, and the compression ice machines at that time had an attachment by which liquefied ammonia gas could be made from aqua ammonia. Aqua ammonia of great purity was not available and the quality of liquefied ammonia gas made by non-chemists with simple apparatus in the ice plant left much to be desired.

In a paper read before this Institute on the occasion of its first annual meeting, I gave a full account of the methods of analysis and the standards of purity of liquefied ammonia gas up to 1908; and from this account it would seem that in early times 2 per cent impurity, or even more, was quite the rule. But in those times the efficiency of refrigerating plants was low. They were largely confined to wort cooling and to cooling of storage rooms in breweries where considerations other than economy were paramount. Only when refrigerating machinery was utilized for making ice in competition with natural ice, was greater efficiency demanded, and this called for purer ammonia.

Refrigeration is not a chemical industry, and for that reason chemists, as a rule, are not familiar with the details of ice plants. But the importance of chemical purity of the refrigerating agent cannot be fully understood without reference to some details of the plant in which it is used, and for this reason a few words would seem justified to explain the function of those parts of the apparatus which have a bearing on the action of ammonia in ice machines. If these are well understood, the importance of the purity of the ammonia charge will become apparent and will be easily appreciated.

In utilizing ammonia, the latent heat required for evaporation of liquid ammonia is employed for the production of "cold."

Liquid ammonia has a boiling point of -28°F . at atmospheric pressure. Its latent heat of evaporation at 0°F . is about 555 B. T. U., and this heat is readily extracted from surrounding bodies having a higher temperature than -28°F ., thus producing "cold," which by suitable apparatus may be utilized for the production of ice or for refrigeration.

The general arrangement of a refrigerating plant is such that liquid anhydrous ammonia is evaporated at a low pressure and a corresponding low temperature in a closed vessel which is submerged in a medium like brine or air. In evaporating at low temperature, the ammonia extracts heat from this medium, thereby lowering its temperature. The resulting ammonia vapors are again reduced to the liquid state by applying pressure and subsequent cooling in a condenser, and the liquid anhydrous ammonia is returned to the cycle of operations.

Refrigeration by ammonia is therefore a physical process and in theory the chemical composition of ammonia in the cycle of operation remains unchanged. The transformation of ammonia from the liquid to the gaseous state and vice versa can go on indefinitely and, theoretically, a given amount of ammonia can produce an infinite amount of "cold."

Any set of apparatus constituting a refrigerating plant using ammonia for an agent includes, therefore, a device in which liquid ammonia is evaporated and a device to reduce ammonia from the gaseous to the liquid state. The first operation, as a rule, takes place in a pipe-coil which is submerged in the medium which is to be cooled. The second operation can be carried out in different ways, and from the method employed, refrigeration plants are classified as absorption or compression plants.

In absorption machines the ammonia gas is absorbed in cold, weak aqua ammonia to make strong aqua ammonia of about 30 to 35 per cent. This operation is carried out in the absorber. The resulting strong aqua ammonia is forced by a pump into the retort or boiler to be heated to about 150°C ., whereby it splits into weak aqua ammonia, 15 to 18 per cent, and hot ammonia gas standing under a pressure of 150 to 250 lbs.

The hot gas under this high pressure is led into the condenser to be cooled and thereby liquefied, producing in good plants liquid ammonia of 95 to 98 per cent purity, the balance being water, which had evaporated with the ammonia. The weak aqua ammonia is returned to the absorber.

In compression machines, the ammonia gas coming from the evaporating or freezing coil is taken by suction into the ammonia pump, whereupon it is compressed to 150 to 250 lbs. pressure per sq. in.; the gas, hot from compression, is delivered to the cooler or condenser to be liquefied to ammonia of approximately 100 per cent purity, which is to be delivered again to the freezing coil, thus completing the cycle of operation.

Comparing the principles involved in absorption and compression machines, it is apparent that apparatus in which evaporation of liquid ammonia takes

place at low temperature and low pressure, and the condenser or cooler in which hot ammonia gas of high pressure is reduced to the liquid state, are alike for both types of refrigerating machines. The expansion valve between the two apparatus and the valves in the pump separate the high-pressure side from the low-pressure side of the machine.

In compression machines the ammonia pump handles ammonia in the gaseous state. The pump is large on account of the great volume of ammonia gas

FIG. I

and its suction side has the same function as the absorber in absorption machines. The compression side has the same function as the aqua ammonia pump and the retort or boiler in absorption machines combined, and it delivers ammonia gas under high pressure to the condenser or cooler. In absorption machines the ammonia pump is comparatively small, since it handles ammonia in the liquid state, viz., in the form of aqua ammonia which has a smaller volume than the equivalent amount of ammonia gas. The pump operates on cold aqua ammonia and does not require lubrication of the pistons.

In compression plants, the ammonia pump is large, operates on hot ammonia gas, and requires generous lubrication of cylinder pistons. Therefore, in compression machines, the lubricants require serious attention.

The arrangement of the fundamental apparatus in both types of machine is illustrated by the diagrams Figs. I and II.

The object of both types of plant is to abstract heat from the low pressure or evaporating side and to deposit the same heat at the high pressure or con-

FIG. II

denser side. This transfer is accomplished by evaporating liquid ammonia at low temperatures, subsequently compressing the resulting ammonia vapors either by application of heat in the retort of absorption machines, or by application of power in compression plants, and to deposit the heat which was extracted at the low-pressure side in the condenser on the high-pressure side, whence it is carried off by cooling water which runs through the condenser.

The amount of heat used in the retort of an absorption machine or the amount of power consumed in a compression plant multiplied by a constant is a measure of the amount of refrigeration actually produced. The value of this constant is the product of many factors, one of which is the free and ready evaporation and condensation of ammonia in the machine. All other conditions being equal, the evaporation and condensation of liquid ammonia goes on most freely if the ammonia is pure. If it contains substances either in suspension or in solution, which retard evaporation or which cause ammonia to boil only in a superheated condition, or which retard the transmission of heat to the ammonia, then the efficiency of the machine is impaired. For this reason ammonia of high purity will produce better results than impure ammonia.

FIG. III

Many impurities which retard evaporation are soluble in ammonia and are less volatile than liquefied ammonia gas. For this reason they may be detected by the evaporation test. An account of this test was given in an earlier paper (*Transactions I*, page 133). But there are many substances less volatile than ammonia, which are harmless and do not impair the speed of evaporation, and yet show up in the evaporation test. To distinguish between harmful and harmless impurities in this regard, the apparatus shown in Fig. III was used to measure the time of evaporation of a definite quantity of liquid ammonia under constant conditions. The apparatus is made of glass and consists of a cylindrical evaporating vessel, A, graduated on its side and having at its lower end a

narrow tube, *B*, in which liquid residues from evaporation may accumulate. The upper part of *A* is drawn out to a small cylindrical part, *C*, with tube *D* inserted which serves to connect the apparatus with the nozzle of the test valve on the ammonia shipping cylinder. *E* is an outlet tube for discharging ammonia vapors coming from the apparatus. *A* is surrounded by jacket *F*, which is joined to tube *B*, and a piece of sheet rubber having a round opening in the center is slipped over tube *C* and is tied over the upper rim of jacket *F* to make an air-tight connection. The air between *A* and *F* must be dry. The lower part of the tube *B* is surrounded by an evacuated bulb, *H*, and the entire apparatus is set in a bath of a 20 per cent solution of calcium chloride, *I*, provided with agitator, *K*, and thermometer, *L*, which serve to maintain a uniform temperature in the apparatus. The calcium chloride solution is contained in a glass jar, *M*, which stands in a bath of ice water and crushed ice.

In evaporating, the ammonia takes heat from the solution of calcium chloride, which in turn takes heat from the melting ice. The object of the apparatus is to make the transfer of heat to the ammonia uniform, in order to make time the measure of evaporation. Dry air in jacket *F* and the vacuum in bulb *H* being bad conductors, all heat must travel through the glass walls of tube *B* between *a* and *b*, which represents the heating surface of the apparatus. Tube *B* extends into bulb *H* to serve as the receptacle for residues of evaporation, which may accumulate in this place, without reducing the area of the heating surface of the apparatus.

The operation of the apparatus is self-evident. By operating the valves on the ammonia cylinder, the apparatus is filled to the 100 cc. mark, whereupon evaporation of the ammonia takes place regulated by the amount of heat which travels from the calcium chloride solution through the walls of tube *B* to the ammonia.

When the ammonia in *A* is evaporated to point *c*, the time of evaporation is noted, together with the temperature of the calcium chloride bath, whereupon a new charge of ammonia is admitted by filling the apparatus up to the 100 cc. mark, and any number of additional charges of liquid ammonia may be evaporated. In repeating the operation, the impurities in the ammonia are concentrated and the time necessary for the evaporation of successive portions is a measure of the increasing amounts of impurities in the ammonia.

Tables I and II give the results of two series of experiments, one of which is made with pure ammonia, similar to quality *B* in Table III, on page 209; the other with less pure ammonia, resembling in composition quality *H* in the same table.

Comparing the values in the two tables, it would seem that the velocity of evaporation of liquid ammonia is not affected by the presence of such small amounts of impurities as are contained in sample *H*. However, the velocity of evaporation decreases rapidly as soon as the oily material, which separates in increasing quantities from the ammonia in successive tests,

increases in volume, covering part of the heating surface of the apparatus, and the table shows also that by the time the entire heating surface is covered with oily material the velocity of evaporation is reduced by 50 per cent.

Among the substances not soluble in liquid ammonia but always present in compression plants, is lubricating oil from the compressor. Its retarding action rests in its low coefficient of conductivity for heat. If it enters the condenser it coats the inside of the ammonia pipe, but owing to the high temperature the oil is very liquid and the coating is thin. Nevertheless, the thin coating of oil in the condenser retards the transfer of heat, but the amount of retardation is small and can be overcome by increasing the pressure on the discharge side of the ammonia pump. If the plant is operated at 200 lbs. pressure, 5 lbs. of which is used for overcoming the retardation caused by the coating of oil, then the loss of efficiency for the sake of argument may be assumed to be $2\frac{1}{2}$ per cent.

Conditions in the evaporating coil are widely different. The evaporating coil is cold, the oil is thick, the coating of the walls inside the pipes is heavy, and consequently the retardation is large. If in this place the pressure is 15 lbs. per sq. in., and if it must be reduced by 5 lbs. to overcome the retardation in the travel of heat, then the loss of efficiency must be counted as $33\frac{1}{3}$ per cent instead of $2\frac{1}{2}$ per cent, as was the case in the condenser. For this reason the evaporating coil must be kept free of lubricating oil.

TABLE I—EVAPORATING TEST OF LIQUID ANHYDROUS AMMONIA
PURITY SIMILAR TO SAMPLE B IN TABLE III

	TEMPERATURE, DEG. F. AT START			100 cc. Evaporated Duration of Test Minutes	TEMPERATURE DEG. F. AT END			Calculated Time of Evaporation at 15 Lbs. Pressure, 15° F. Minutes
	Air (a)	Water	Brine		Brine	Water	Air (a)	
1914								
July 21	90	38	42	130	28	38	90	...
	90	38	28	140	28	40	90	570
	90	40	28	135	26	38	90	540
	90	38	26	140	26	38	90	549
AVERAGE.....								553
July 22	95	42	46	125	30	42	95	...
	95	42	30	135	28	38	95	559
	95	38	28	140	28	38	95	570
	95	38	28	135	28	38	95	549
AVERAGE.....								559
July 23	95	40	46	125	30	40	95	...
	95	40	30	130	28	40	95	538
	95	40	28	140	28	36	95	570
	95	36	28	140	28	36	95	570
AVERAGE.....								559
July 24	97	42	48	125	28	36	97	...
	97	36	28	135	26	34	97	540
	97	34	26	140	26	34	97	549
	97	34	26	140	26	34	97	549
AVERAGE.....								546
GRAND AVERAGE.....								554
PROBABLE ERROR.....								± 10

(a) Average temperature of air.

NOTE—No residue accumulated in the lower part of tube *B*, therefore any number of evaporations of new quantities of ammonia could be carried out with the same results. Evaporation of the first sample on every day was not considered, because the high temperature of brine made results irregular.

The evaporated ammonia is withdrawn from the freezing coil by the absorber in absorption machines, or by the ammonia pump in compression plants. Here again the efficiency is greatest if the ammonia is pure. If the ammonia is contaminated with gases, which cannot be absorbed by water, then these gases will accumulate in the absorber in the case of absorp-

TABLE II—EVAPORATING TEST OF LIQUID ANHYDROUS AMMONIA
PURITY SIMILAR TO SAMPLE H IN TABLE III

	100 cc. Evaporated				Calculated Time of Evaporation at 15 Lb. Pressure 15° F.			
	TEMPERATURE, DEG. F., AT START	TEMPERATURE, DEG. F., AT END	Duration of Test	Brine Water Air (a)	TEMPERATURE, DEG. F., AT START	TEMPERATURE, DEG. F., AT END	Duration of Test	Brine Water Air (a)
1914	Air (a)	Water	Brine	Minutes	Brine	Water	Air (a)	Minutes
Aug. 15	88	42	52	130	28	38	88	...
	88	38	28	150	26	36	88	540
	88	36	26	150	26	36	88	520
Aug. 17	94	42	50	135	28	38	94	...
	94	38	28	150	28	38	94	560
	94	38	28	150	26	34	94	540
	94	34	26	150	26	34	94	520
Aug. 18	95	40	50	140	28	36	95	...
	95	36	28	150	28	36	95	560
	95	36	28	150	28	34	95	560
	95	34	28	150	28	34	95	560
Aug. 19	93	40	50	140	28	36	93	...
	93	36	28	150	28	36	93	560
	93	36	28	150	28	36	93	560
	93	36	28	155	28	36	93	579
AVERAGE	...	...	...	...	...	...	...	550
Aug. 20	88	48	54	140	28	38	88	...
	88	38	28	155	28	36	88	579
	88	36	28	155	28	36	88	579
	88	36	28	155	28	34	88	579
Aug. 21	90	50	58	140	28	36	90	...
	90	36	28	155	28	36	90	579
	90	36	28	160	28	36	90	597
	90	36	28	160	28	36	90	597
Aug. 24	75	48	58	155	28	38	75	...
	75	38	28	195	28	36	75	...
	75	36	28	200	28	36	75	747
Aug. 25	70	50	58	205	28	36	70	...
	70	36	28	205	28	36	70	765
Aug. 26	81	40	52	205	28	36	81	...
	81	36	28	220	28	36	81	821
Aug. 27	75	50	58	225	28	36	75	...
	75	36	28	235	28	36	75	877
Aug. 28	70	40	48	250	28	36	70	...
	70	36	28	260	28	36	70	971
Aug. 29	...	44	50	265	38	36	...	...
	...	36	28	270	28	36	...	1008
Aug. 31	...	44	50	260	30	36	...	...
	...	36	30	275	30	36	...	1063
Sept. 1	...	42	52	270	30	34	...	...
	...	34	30	285	30	36	...	1102
Sept. 2	...	46	54	280	30	34	...	...
	...	34	30	295	30	34	...	1141
Sept. 3	...	36	38	285	30	36	...	...
	...	36	30	295	30	36	...	1141
Sept. 5	...	50	54	290	30	36	...	...
	...	36	30	295	30	36	...	1141
PROBABLE ERROR	...	...	...	±2.5	...	...	...	±10

(a) Average temperature of air.

tion machines and cause pressure, which prevents the ready flow of ammonia gas towards the absorber, whereby the efficiency of the plant is reduced.

In the case of compression machines, any gases not ammonia will fill space in the cylinder of the ammonia pump, and will reduce the efficiency of the pump in direct proportion to the volume of such gases present. If the ammonia gas contains 10 per cent of such gases, then the efficiency of the pump will be reduced by 10 per cent.

More serious is the presence of non-condensing gases in ammonia at the compression side of the machine. In both absorption and compression plants, the gas under high pressure enters the condenser to be liquefied. Liquefaction depends upon the pressure and temperature in the condenser. The temperature being largely invariable since it is dependent upon the temperature of the cooling water, the efficiency of a given plant depends largely upon the pressure of the ammonia gas alone.

Pure ammonia gas condenses to liquid ammonia at lowest pressure at a given temperature. If the ammonia gas is contaminated with gases of a non-condensing nature then the pressure necessary for condensation of the ammonia in the gas mixture is increased, according to well-known physical laws. The increase of pressure is in direct proportion to the amount of non-condensing gases present. If the ratio of am-

monia to other gases is 1 to 1, then twice as much pressure is required for its condensation as for the condensation of pure ammonia.

This applies both to absorption and compression machines. It becomes serious if the space which is occupied by the gases in the condenser is small. Double pipe condensers, which are mostly used, have a very small condensing space, measuring at an average 12 cu. in. per ft. of pipe. The ammonia in a gas mixture forced into a condenser is liquefied and withdrawn while the contaminating non-condensing gases remain, gradually filling the condenser in cumulative action and paralyzing its efficiency. For this reason ammonia of high purity will produce superior results.

The non-condensing gases mixed with ammonia may be air and in this case they are easy to detect. An apparatus for measuring them is published in Vol. VI, p. 214, of our *Transactions*. But there may be other impurities in ammonia, which, liquid in themselves, may produce non-condensing gases in ice machines, and many of these substances are difficult to detect by analysis. Therefore, the consumer must largely rely upon the reputation of the ammonia manufacturer who stands for the quality of his goods.

There is another source from which non-condensing gases may develop in compression machines, and it must be well understood that not in all cases is the quality of ammonia responsible for the presence of non-condensing gases in the machine. The oil used for lubricating the compressor mixes intimately with the ammonia and if it contains substances, which at temperatures prevailing in the machine develop permanent gases, then these constituents of the oil act in the same manner as if they were brought in with the ammonia charge. Fortunately most oil is good in this respect; and particularly the cheaper grades of compressor oil give good satisfaction. However, there is oil on the market which is undesirable, and operators of ice machines do well to make sure of the good quality of the oil they use in their machines.

A simple apparatus for testing oil in this respect is represented by Fig. IV. It is operated as follows:

FIG. IV

With the stopper removed, the bulb tube is filled entirely with the oil which is to undergo the test, whereupon the stopper is firmly inserted and the excess oil removed from the funnel over the stopper. Upon heating in a metal bath, undesirable oils will develop gases which will accumulate under the stopper, while an equivalent volume of oil is forced through

the capillary tube into the funnel over the stopper and the volume of gas may be measured by the graduation on the tube.

If non-condensing gases accumulate in the machine, it becomes necessary to remove them and the operation of doing this is called purging.

Purging is generally done by opening a small valve on the top of the condenser, or absorber, or both. The gases which always contain a large proportion of ammonia may be led by a tube under water, whereby ammonia is absorbed, the permanent gases rising in bubbles to the surface of the water. If no bubbles form, all the non-condensing gases are removed, and purging is completed. Another way of purging is to let the gases escape into the air and ignite them by a torch, in which case they burn with a luminous flame which dies out as soon as pure ammonia flows from the orifice. With pure ammonia in the machine, purging may be done at long intervals of time, while with impure ammonia daily purging becomes a necessity.

There is finally a class of impurities found in ammonia which causes corrosion of iron, from which ice machines are made. This occurs more frequently in absorption plants, where corrosion often destroys parts of machinery, causing leaks, and subsequent loss of ammonia during operation.

Acetic acid, acetonitrile, and similar compounds belong to this class of impurities, and they are frequently found in aqua ammonia. A small amount of

acetic acid can corrode large quantities of iron by hydrolysis, since the acid always is regenerated. The chemical action on parts of apparatus is illustrated by two tubes represented in Fig. V and Va. Both tubes were used for four years in two absorbers, the one in pure, the other in impure, aqua ammonia. The one has lost hardly any of its weight, while the other is corroded to a thin shell.

FIG. V

FIG. Va

In absorption machines the heating coils in the retort are most seriously affected by impure ammonia.

Fig. VI represents the lower part of a retort containing a double heating coil. The coil is made from 1 1/4-in. extra strong iron pipe, and weighs about 1200 lbs. If used with pure aqua ammonia, it will last many years, while with impure ammonia frequent renewal becomes imperative. I hold records about coils of this particular size, which in a single year lost as much as 100 lbs. of their weight by corrosion if used with impure ammonia, and I have records of other coils of the same size which were used for as much as 10 years with pure ammonia under the same conditions as the first-mentioned coils and which lost less than 5 lbs. of their original weight.

How seriously the efficiency of an ice plant can be affected by impure ammonia is strikingly demonstrated by the results which were obtained in the operation of two new and identical absorption ice machines, operated in parallel and independently of one another by the same steam plant, by condensing water of the same temperature, and by the same set of engineers, but charged with an equal quantity of ammonia of different purity. Both qualities of ammonia were goods offered in the regular market and were purchased by the manufacturer of the two ice machines for the purpose of making a comparative test of the ammonia. The operations were conducted under the direction of the manufacturer of the ice machines and by the proprietors of the

FIG. VI

plant, who were disinterested parties. Each of the two ice machines had a capacity of 50 tons and there was an independent ice tank for each machine. The test was run over a period of almost 17 months, beginning June 6, 1914, and terminating October 31, 1915.

The first charge of each machine consisted of 16,500 lbs. aqua ammonia, 26° Bé., and 3855 lbs. liquid anhydrous ammonia. During the 17 months of operation 375 lbs. aqua ammonia 26° Bé. and 775 lbs. liquid anhydrous ammonia were added to replenish the charge in Plant No. 1, and on Oct. 31, 1915, after 17 months' operation, the charge was approximately of the same strength as at the beginning of the test run. The machine was operated 24 hrs. per day except between seasons, when it was run in day time only, and in winter, when it was shut down. Ice was drawn

at the rate of 55 tons per day during about 8 months and refrigeration was supplied to the ice-storage room estimated to be equivalent to 3 tons of ice per 24 hrs. in the warm season of the year. The plant ran regularly about 15 per cent over rated capacity. A total of 15,862 tons of ice was pulled, and counting the refrigerating done as equivalent to 1000 tons, 16,862 tons of ice were produced in 17 months at an expense for ammonia amounting to 1.27 cents per ton of ice. Nineteen tons of ice were made for every pound of ammonia lost in operating the plant.

No serious leaks were observed in the plant. Small quantities of permanent gases were burned off during the first weeks of operation, giving a flame about 3 in. long from a $\frac{3}{8}$ -in. pipe. No gas was purged off during the following four months and in the second summer a flame of only about $\frac{1}{2}$ in. length could be burned from the purge tube at intervals of time and then only for a few minutes.

A sample of aqua ammonia drawn from the machine after a 17 months' run was clear as water and it is believed that no corrosion whatever has taken place inside the plant. This, however, can be confirmed only by opening the apparatus, which will probably not be necessary for several years to come.

The result of this run is remarkable if it is compared with the result in Plant No. 2. This plant was started June 22, 1914, 18 days later than Plant No. 1. With the same quantity of ammonia, bought from a different manufacturer and used for the initial charge, Plant No. 2 could produce only 42 to 44 tons of ice while Plant No. 1 had made 57 tons. Upon the addition of 1000 lbs. anhydrous ammonia, 50 tons of ice could be made per day in No. 2.

From June 22, 1914, to November 1, 1915, that is, in about 16 $\frac{1}{4}$ mo., 13,183 lbs. aqua ammonia, 26° Bé., and 3484 lbs. anhydrous ammonia were used in addition to the initial charge, and at the end of the period the ammonia charge in the machine was about 1000 lbs. short on ammonia. 11,308 tons of ice had been made during the period and the cost of ammonia per ton of ice was 15.16 cents, as against 1.27 cents in Plant No. 1. One and one-third tons of ice were made for every pound of ammonia lost in operating the plant.

Serious leaks were observed after a few weeks' operation in the screw connections of the pipes and condensers, caused by corrosive action of the ammonia. Large quantities of permanent gases were burned off daily during the entire period of operation, giving a flame of as much as 3 in. diameter, and over 24 in. long, and this flame would burn from 20 to 30 min. at a time. The excessive consumption of ammonia was caused by leaks and purging.

A sample of aqua ammonia drawn from the machine after 16 months' operation was dark and dirty, and no doubt considerable corrosion had taken place inside the apparatus.

Plant No. 1 had made during the test period an equivalent to 16,862 tons of ice, while Plant No. 2 made 11,308 tons, a deficiency of 33 per cent, and this

deficiency must be attributed alone to the difference in quality of the ammonia charge.

The consumption of coal in Plant No. 1 was ascertained to be one ton of Illinois coal to eight tons of ice, while in Plant No. 2 only 5 $\frac{1}{2}$ tons of ice were made per ton of coal, consumed under the boiler.

Similar differences in efficiency were experienced in many plants, which led to the belief that the quality of the ammonia charge had an important bearing upon the operation of ice plants. There were no methods of analysis known to be delicate enough for the purpose of differentiating between the quality of different brands of ammonia, and it seemed to be of sufficient importance to have methods of analysis developed even at great cost for the best of the refrigerating industry. Upon the request of the American Association of Refrigeration, Congress appropriated \$30,000 to be put to the credit of the Bureau of Standards, which sum was to be used for the development of methods of analysis of commercial ammonia and for the determination of physical constants of refrigeration.

The composition and testing of commercial liquid ammonia was admirably investigated by E. C. McKelvy and C. S. Taylor, both of the U. S. Bureau of Standards, Washington, D. C., by experiments equal in accuracy to determinations of atomic weights.

A progress report on the result of 2 years' work was presented at the twelfth annual meeting of the American Society of Refrigerating Engineers in December, 1916, and published in their journal for March, 1917.

The report describes in detail methods of sampling and methods of analysis for the quantitative determination of, first, non-condensing gases; second, residue on evaporation; third, volatile impurities containing carbon; fourth, water; fifth, pyridine; sixth, acetonitrile and ammonium acetate; and seventh, direct determination of ammonia.

McKelvy and Taylor made by these methods a series of comparative tests on eleven samples of liquid anhydrous ammonia made by ten different manufacturers and tabulated the results. The eleven samples were marked by letters of the alphabet from A to S. Samples A to H represented eight standard American brands provided in 50- to 100-lb. cylinders. They were obtained either by purchase in the open market, or by purchase or donation from manufacturers, and are believed to represent fairly well the material now used in the refrigerating industry. Samples K, L and LL were of German origin, L having been purchased in 1906. Sample M was an American product purchased in 1907. Sample S was prepared from Sample B by several fractional distillations, the first of which was made from metallic sodium.

The results of the comparative tests are given in Table III, opposite the letter indicating the origin of the sample. The column headings show the nature of the test and the manner of expressing the results.

As to the limit of accuracy of the figures given in

the table, it was found that in the case of volatile carbon compounds the results were too low. Fifty-eight grams of pure ammonia, mixed with 3 mg. acetonitrile, yielded 95 per cent of the carbon in the combustion test, while 58 g. of ammonia mixed with 15 mg. acetonitrile yielded only 67 per cent of the calculated amount of carbon dioxide, owing to incomplete combustion in the experiment. For this reason, the values given in the table for Samples *B* and *K* are fairly correct, while the amounts of carbon dioxide obtained from other samples were much too low, probably by 40 to 100 per cent. In the case of pyridine, the limit of accuracy was found to be 1 in 100,000,

TABLE III—COMPOSITION OF LIQUID ANHYDROUS AMMONIAS

Sample	NON-CONDENSING GAS		Composition			Residue on Evaporation By Weight Per cent	Volatile C Compounds G. CO ₂ Per 100 g. NH ₃	WATER		
	In Liquid Cc. Per 100 g.	In Gas Cc. Per 100 g.	N ₂ Per cent	O ₂ Per cent	H ₂ Per cent			G. CO ₂ Per 100 g. NH ₃	Method KOH Per cent	Method CaC ₂ Per cent
<i>A</i>	7	..	69.1	30.9	0.0	0.012 <i>h</i>	0.019	0.006	0.013	
	..	26	86.7	13.3	0.0	0.007 <i>l</i>	0.007	0.001		
<i>B</i>	4	..	70.8	29.2	0.0	0.009 <i>h</i>	0.002	0.007	0.042	
	..	9	70.0	30.0	0.0	0.011 <i>l</i>	0.011	0.008		
<i>C</i>	6	..	70.3	29.7	0.0	0.008 <i>h</i>	0.051	0.007	0.030	
	..	8	69.4	30.6	0.0	0.008 <i>l</i>	0.008	0.005		
<i>D</i>	6	..	68.4	31.6	0.0	0.014 <i>h</i>	0.029	0.006	0.030	
	..	12	72.6	27.4	0.0	0.017 <i>l</i>	0.017	0.004		
<i>E</i>	6	..	65.0	35.0	0.0	0.011 <i>h</i>	0.019	0.006	0.030	
	..	11	74.0	26.0	0.0	0.010 <i>l</i>	0.010	0.006		
<i>F</i>	15	..	67.0	28.7	4.0	0.015 <i>h</i>	0.061	...	0.026	
	..	8032	80.1	19.9	0.0	0.022 <i>l</i>	0.022	...		
<i>G</i>	6	..	70.0	27.0	3.0	0.025 <i>h</i>	0.032	0.007	0.026	
	..	9	68.0	26.0	6.0	0.100 <i>l</i>	0.100	0.009		
<i>H</i>	6	..	66.7	33.3	0.0	0.062 <i>h</i>	0.902	0.010	0.027	
	..	11	66.7	33.3	0.0	0.134 <i>l</i>	0.134	0.010		
<i>K</i>	7	..	69.0	31.0	Trace	0.276 <i>h</i>	0.004	0.011	0.80	
	..	19	80.0	20.0	Trace	0.300 <i>l</i>	0.300	0.032		
<i>L</i>	9	..	77.5	22.5	0.0	0.533 <i>h</i>	0.497	0.041	0.50	
	..	5680	99.4	0.6	Trace	0.540 <i>l</i>	0.540	0.069		
<i>LL</i>	15	..	79.0	21.0	0.0	0.318 <i>h</i>	0.103	0.053	0.33	
	..	1870	99.3	0.7	0.0	0.230 <i>l</i>	0.230	0.040		
<i>M</i>	..	..	..	..	..	0.040 <i>h</i>	0.014	...	...	
	..	..	..	..	..	0.051 <i>l</i>	0.011	...	...	
<i>S</i>	..	..	..	..	..	0.000	0.000	...	0.008	

(*h*) Evaporation at room temperature. (*l*) Evaporation at low temperature.

and for acetonitrile and ammonium acetate quantities less than 5 in 100,000 could not be detected.

In addition to the results in the table, McKelvy and Taylor point out the following data of interest:

Sample *F* contained a trace of pyridine and sample *H* 0.02 per cent. The German Samples *L* and *LL* contained 0.015 per cent and 0.005 per cent, respectively. All others contained less than 0.001 per cent.

In the samples showing a low residue on evaporation (*A* to *E*), the residue consisted of a reddish film hardly visible. For the other samples at most a brownish drop of oily liquid was left, and only for Samples *K*, *L* and *LL* could the volume of the results have been measured. The percentage of iron oxide in the residue was greater, the smaller the amount of residue in the sample.

Sample *F* contained 0.005 per cent ammonium acetate or acetate-forming substance, and Sample *L* a trace. All others contained less than 0.005 per cent.

The results of the combustion tests showed a marked difference in the various samples, but in practically all of the tests McKelvy and Taylor observed that no carbon dioxide appeared in the absorber until at least 95 per cent of the liquid had evaporated.

In making this observation, the Bureau of Standards in 1916 disclosed the fact that small quantities

of volatile carbon compound can be concentrated into a small volume of liquid anhydrous ammonia by fractional distillation. The Badische Company observed the same fact and patented its invention in 1913. The same process was discovered and put into operation in 1892 in these works and has been in successful operation ever since. While inspecting our works this afternoon you will have an opportunity of seeing the first apparatus used in 1892 and the present plant comprising 5 compressors and 3 stills capable of redistilling 25,000 lbs. of liquid anhydrous ammonia per day of 24 hours. The product corresponds in quality to Sample *B* in the table, the volatile carbon compounds of which are so small that by burning 100 g. ammonia only 0.002 g. carbon dioxide could be obtained, which indicates that less than 0.001 per cent volatile carbon compounds could have been in the ammonia.

Sample *K* in the table, which comes nearest to *B*, was ammonia made in Germany by the Haber process and was evidently redistilled since the Badische Company holds a patent for purifying ammonia from the Haber process by fractional distillation.

The importance of this investigation is emphasized if I state that in the test run with the two 50-ton machines described in this paper, Plant No. 1 was charged with ammonia which in quality was equal to Sample *B* in the table. The aqua ammonia for the prime charge of this machine was also made by saturating pure distilled water with ammonia of purity *B*.

Plant No. 2 was charged with aqua ammonia of unknown purity. The same brand, however, has given good satisfaction in other instances. But I have reason to believe that the liquid anhydrous ammonia in this charge was similar in quality to Sample *H*, and from this the conclusion might be drawn that the difference in efficiency of the two plants was caused by the difference in purity of the ammonia charges and more particularly by the presence of volatile carbon compounds in the ammonia.

It is to be hoped that this progress report of the Bureau of Standards may soon be followed up with a complete account. The remaining part of the report will include an investigation and analysis of aqua ammonia, a most difficult problem, and at the same time, a problem of the greatest importance for the operation of absorption ice machines. At the present we possess no method of analysis sensitive enough to ascertain small quantities of impurities in aqua ammonia, and enormous sums of money are constantly being lost in the operation of absorption ice machines on account of impure ammonia.

The only way to minimize these losses at the present time would seem to be in using liquid anhydrous ammonia of known purity and pure distilled water for charging absorption plants. But attention should be paid to the quality of distilled water, which rarely is made of sufficient purity to answer this purpose. Here in St. Louis, we are fortunate to have a supply of city water which upon a single distillation yields an excellent product for use in making aqua ammonia. In the city water plant, Missouri River

water is first purified by sedimentation, after the suspended matter has been coagulated by sulfate iron and lime. A subsequent filtration by sand filters removes the last suspended matter and oxidation with chlorine removes bacteria.

From water obtained by distillation of St. Louis city water, and liquid anhydrous ammonia of purity *B*, my company is manufacturing pure aqua ammonia for use in absorption ice machines, and aqua ammonia used in the test run in Plant No. 1, which was described before, was aqua ammonia of this purity.

Reverting to the question of analysis of aqua ammonia, it is believed that the quick detection of minute quantities of volatile substances which render aqua ammonia unfit for use in refrigerating machines will hardly be accomplished by chemical analysis. It is most likely that methods have to be resorted to which are based upon physical principles and which reveal actions of such impurities, although they do not disclose their identity. In looking over the literature on the subject, I found a statement by G. Tammann in his investigation on vapor tensions¹ that apparently the increase of vapor tension of volatile substances following a decrease in space, which is occupied by the same vapors, is caused by minute impurities, and it would seem possible to use this observation for a method of testing volatile substances for purity.²

This remark is prompted by the observation of A. Wullner and O. Grottrian³ that the vapor tension of volatile substances increases if the vapor volume is decreased.

Wullner and Grottrian found the increase of vapor tension for water smaller than for other volatile substances, yet it would be 5-10 mm. if the vapor volume was reduced from $\frac{1}{6}$ to $\frac{1}{10}$ of the original volume.

G. Tammann has repeated these experiments, and has found that there is no increase of vapor tension caused by decrease of vapor volume for water, *if it is pure*, and he succeeded in making water of sufficient purity to prove this fact.

For ether and carbon bisulfide he could materially reduce this irregularity by purifying the substances, but he could not make them sufficiently pure to show the same tension at varying volumes.

From this Ostwald⁴ draws the conclusion that no substance except water has ever been made of absolute purity.

G. Tammann then suggests that this observation might be used for a method of testing volatile substances for purity and Ostwald states⁴ that one part benzene in 10,000 parts of water can be detected in this manner.

It has occurred to me that these observations may be used for determining volatile impurities in aqua ammonia in the following manner:

Two barometers are combined in one apparatus, one of which is charged over mercury with a solution of pure sulfate of ammonium and pure water, the other with aqua ammonia, which is to be tested, and which previously was neutralized with pure sulfuric acid to make a solution of ammonium sulfate in water of the same concentration as the solution charged into the first barometer; and then the relative vapor tension in the two barometers at various temperatures is determined.

To prove the possibility of this method, apparatus shown in Fig. VII was constructed, having two barometers in a narrow space allowing of uniform heating of both barometers.

Two barometers were made from one length of glass tubing which was equally wide at both ends. The tube was drawn out to a point in the center and both points were closed. Therefore both barometers were equally wide near the closed end of the tube and 1 cc. of mercury filled 22 mm. of the barometer tubes. For making the test both tubes were filled with mercury and the air was removed by repeated evacuation, and filling up with mercury. A 25 per cent solution of pure sulfate of ammonium in water was prepared from which air was expelled by boiling, and methyl orange

was added to prove acidity. 2.5 cc. = 2.825 g. of this solution were introduced into each barometer, and in Barometer *B* 0.015 g. benzene enclosed in a small flask was also inserted, whereupon the following readings were taken at various temperatures and various pressures.

Table IV shows that 0.003 per cent benzene can

FIG. VII

¹ *Mémoires de l'Académie des sciences de St. Petersburg* VII, serie tome 35, No. 9 (1887), 18.

² Compare Ostwald, *Allgem. Chemie*, I, 306-309.

³ Wiedemann, *Annalen*, 11 (1880), 600.

⁴ *Allgem. Chemie*, I, 309.

easily be detected in 25 per cent solution of ammonium sulfate by use of this apparatus:

Temp. Deg. C.	TABLE IV	
	Difference in Barometer B - A = mm.	1 mm. Indicates Benzene Per cent
20	52	0.0106
27	77	0.0071
35	105	0.0051
45	148	0.0038
60	184	0.0030
70	200	0.0027
80	215	0.0026

I am well aware that the apparatus and experiments which I have presented to you are in no way exact and complete in the way physicists will look at them, and I would hesitate indeed to present them for publication in a physical journal. In no way can they compare with the investigations of H. C. Dickinson and N. S. Osborne of the U. S. Bureau of Standards on the constants of refrigeration. But incomplete as they are, they have served me as guides in the manufacture of pure ammonia for use in ice machines, and I find satisfaction in the assurance that the most painstaking investigations of McKelvy and Taylor have confirmed the fact that commercial liquid anhydrous ammonia of such purity is made that it is more worthy of the designation "chemically pure" than many other chemicals which are sold at a high price as chemicals of highest purity.

4320 WASHINGTON BOULEVARD
ST. LOUIS, MISSOURI

TESTING NATURAL GAS FOR GASOLINE

By G. G. OBERFELL

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CASING-HEAD GAS

A very complete description of the methods for testing natural gas for gasoline is contained in the publication by G. A. Burrell and G. W. Jones.¹

The objections to the various methods have been well stated in this publication. Owing to the fact that tests with the portable absorber seem to be more practical, that method has been preferred in most of the test cases carried out for the Ohio Fuel Supply Company. The main objection to the use of the portable absorber in field testing is the effect of pressure on the yield.²

In order to meet the requirements for a method that would give the content and gravity of gasoline in natural gas, it was deemed advisable to modify the absorption method so as to meet all conditions of pressure encountered in field testing. The pressure therefore chosen was atmospheric.

Tests have shown that the allowable saturations of oil with gasoline for complete extraction of gasoline depend upon the gas pressure, the temperature of the oil, the gasoline content of the gas, and the type of absorber. The four-coil type of absorber designed by P. M. Biddison³ gives a greater yield in most cases in tests with casing-head gases than the absorber with one coil. Experience has shown that the four-coil type of

absorber when used in testing casing-head gas gives practically the same yield as the apparatus used in these experiments, providing a low percentage saturation of oil with gasoline is maintained.

The absorber (Fig. 1) used in these experiments was designed so as to give sufficient contact of oil and gas in order to completely remove the gasoline. The absorber is cylindrical in form and made of 22 gauge galvanized iron. It is 10 in. in diameter and 24 in. in length. The ends of the absorber should be conical. The ends are fitted with quarter-inch nipples attached by a boss. Quarter-inch globe valves or quarter-inch cocks are attached to the nipples. The dimensions chosen give the absorber a capacity of about 1 cu. ft.¹

FIG. 1—CUBIC-FOOT ABSORBER

The absorber was calibrated by weighing with water and checked against the meter made by the American Meter Company and used for determination of heating values of gases.

METHOD OF OPERATING

One end of the absorber is attached to the gas supply by means of rubber tubing. The absorber placed in a vertical position is then purged for 30 min. Connection with the gas supply is made at the top in case the gas is lighter than air, or at the bottom in case the gas is the heavier. In either case the last 15 min. for purging should be made at the top so as to expel small amount of oil left from the previous test. The valves

¹ "Industrial Gas Calorimetry," Bureau of Standards, *Technologic Paper* 36, 35.

¹ "Methods of Testing Natural Gas for Gasoline Content," Bureau of Mines, *Technical Paper* 87.

² *Proceedings of The Natural Gas Association*, 8, 1916.

³ *Natural Gas Journal*, 1916.