Conversion of Potassium Chloride to Potassium Nitrate by the Reaction of Nitrogen Dioxide

Going Yim

Dept. of Inorg. Mat'ls Eng., Pai Chai University

439-6 Doma-dong, Seo-gu, Taejon 302-735, Korea

Potassium Chloride로 부터 Nitrogen Dioxide 반응에 의한 Potassium Nitrate로의 전환

임 굉

배재대학교 무기재료학과

Abstract : The direct conversion of solid potassium chloride to solid potassium nitrate by the reaction of the chloride with gaseous nitrogen dioxide is suggested for the preparation of potassium nitrate. Thermodynamic calculations indicate that the free energy change is favorable at ordinary temperatures and that the reaction is exothermic.

Experiments are described in which it was found that the reaction takes place at ordinary temperatures in the presence of a small amount of water with good yield. Nitrosyl chloride is produced simultaneously.

염화물을 이산화질소기체로 반응시킬때와 같이 고체 염화칼륨으로 부터 고체 질산칼륨으로의 직접적 인 전환이 질산칼륨의 생성을 암시하고 있음을 확인하였다. 또 열역학적 추정에 있어서 자유에너지 변화는 상온에서 유리하며 발열반응을 보여준다. 그리고 높은 수율과 함께 적은 양의 물존재로 인하 여 상온에서 반응이 일어나며 반응생성물에서 염화니트로실이 동시에 생성되고 있다.

Key words : Potassium Nitrate, Nitrogen Dioxide, Nitrosyl Chloride, Conversion, Thermodynamical Calculation.

I. Introduction

Potassium nitrate is used in the following applications : (a) in pyrotechnics; (b) in explosives; (c) in matches; (d) in blasting powders; (e) in reagent; (f) to modify burning properties of tobacco; (g) in glass manufacture; (h) in metallurgy; (i) as oxidizer in solid rocket propellants; (j) in food preservative; (k) as color fixative in pickling meats; (l) in anaphrodisiac; (m) in tempering steel; and (n) in specialty fertilizer.

In particular many workers have demonstrated the superior properties of potassium nitrate as a fertilizer material. Among the more promising salts for use in concentrated fertilizer mixtures is potassium nitrate[1]. This salt contains two fertilizing elements, is much less hygroscopic than other fertilizer nitrates, and has recognized merits as a fertilizer.

The present paper describes preliminary work on a method for its preparation from solid potassium chloride and nitrogen dioxide (or nitrogen peroxide), the cheapest forms of potash and nitric nitrogen.

Mehring, et al.[2] have shown that, when nitrogen dioxide reacts with a saturated potassium chloride solution, hydrogen chloride is evolved, and a solution containing potassium nitrate and nitric acid is formed. When, however, in cyclic operation, the acid concentration reaches a certain value, nitrosyl chloride is formed and comes off with the hydrogen chloride.

Now if nitrogen dioxide could be made to react with soild potassium chloride, there is presented the possibility of converting the solid chloride directly into the solid nitrate and of obtaining all the chlorine as nitrosyl chloride according to the reaction:

$$2NO_2(g) + KCl(s) \;=\; KNO_3(s) + NOCl(g)$$
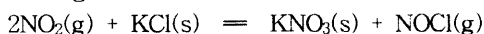
Thermodynamic calculations indicate a free energy change favorable to the occurrence of the foregoing reaction at ordinary temperatures, and the experiments described later show that in the presence of a little moisture this reaction actually takes place.

II. Thermodynamic Considerations

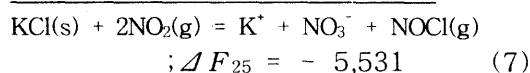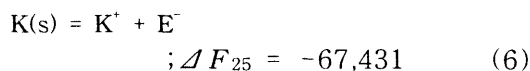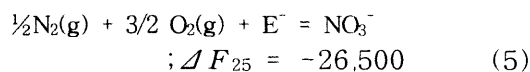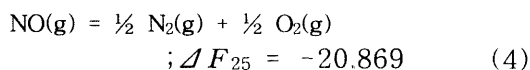In the following calculations 4.184 joules have been taken as equivalent to 1 calorie.

To obtain the free energy change of the reaction,

$$KCl(s) + 2NO_2(g) \;=\; KNO_3(s) + NOCl(g)$$
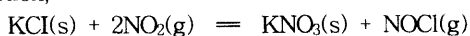
the free energy of formation of KCl(s) was first determined from the free energies of Na(s), K(s), KCl(s), and NaCl(s) by means of the free energy of formation of NaCl(s). Using the data presented in International Critical Tables[3], it is found that $\Delta F_{KCl} = -97,361$.

The free energy of formation of KNO_3 in infinite dilution by the reaction between KCl

and NO_2 is now easily determined.[3]

$$KCl(s) = K(s) + \tfrac{1}{2}\,Cl_2(g)$$
$$;\Delta F_{25} = \;\;\;97,361 \qquad (1)$$

$$NO(g) + \tfrac{1}{2}\,Cl_2(g) = NOCl(g)$$
$$;\Delta F_{25} = \;-\;4,840 \qquad (2)$$

$$2NO_2(g) = 2NO(g) + O_2(g)$$
$$;\Delta F_{25} = \;\;\;16,748 \qquad (3)$$

$$NO(g) = \tfrac{1}{2}\,N_2(g) + \tfrac{1}{2}\,O_2(g)$$
$$;\Delta F_{25} = \;-20,869 \qquad (4)$$

$$\tfrac{1}{2}N_2(g) + 3/2\,O_2(g) + E^- = NO_3^-$$
$$;\Delta F_{25} = \;-26,500 \qquad (5)$$

$$K(s) = K^+ + E^-$$
$$;\Delta F_{25} = \;-67,431 \qquad (6)$$

$$\overline{}$$

$$KCl(s) + 2NO_2(g) = K^+ + NO_3^- + NOCl(g)$$
$$;\Delta F_{25} = \;-\;5,531 \qquad (7)$$
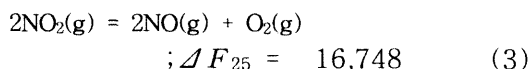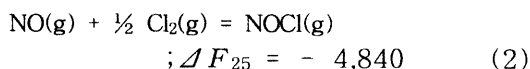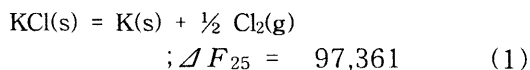
There remains to be determined the free energy change in bringing potassium nitrate in infinite dilution to the solid state or (since the activity of a solute in its saturated solution equals that of the solid solute) to saturation.

The activity of potassium nitrate at the eutectic point (-3℃) is obtained from freezing point data by means of the formula[4]:

$$\log \frac{\sqrt{a}}{m} = \int_0^m - \psi\, d\log m - \frac{\psi}{2.303}$$
$$+ \frac{0.00025}{n} \int_0^m \frac{1}{m}\,\theta\, d\theta \qquad (8)$$

in which $\quad \psi = 1 - \dfrac{\theta}{n\, m\, \lambda}$

The value of the first integral of Equation (8) up to $m = 0.01$ is given by

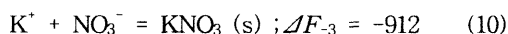$$\int_0^{0.01} - \psi\, d\log m = -\frac{\beta}{2.303\,\alpha}\,(0.01)^\alpha \qquad (9)$$

Where α and β = 0.565 and 0.427, respectively[4], and from $m = 0.01$ to $m = 1.247$ (the molality at the eutectic point) by graphical integration. The value of the second integral is obtained by graphical integration also.

By substitution of the value of a at saturation ($m = 1.247$) from Table 1, in the
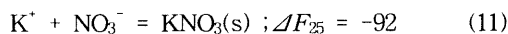
equation[4]

$$\Delta F = RT \ln a$$

it is found that

$$K^+ + NO_3^- = KNO_3 \text{ (s) } ; \Delta F_{-3} = -912 \qquad (10)$$

On the assumption that ΔH for this change of state is constant ($-8,678$ calories)[3] over the small range of temperature, integration of the equation[5]

$$\int_{-3}^{25} d\left(\frac{\Delta F}{T}\right) = -\int_{-3}^{25} \frac{\Delta H}{T^2} \, dT$$
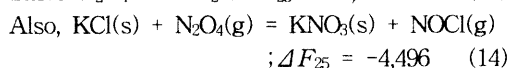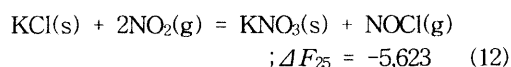
gives $\triangle F_{25} = -107$. On the assumption that the molal heat capacities are constant (-17.20[6] and 21.64[3]), solution of the equation[4,5]

$$\Delta F = \Delta H_0 - \Delta C_P T \ln T + \tau T$$

gives $\Delta F_{25} = -77$. The true value lies somewhere between these two values. Assuming it to be midway[3-7],

$$K^+ + NO_3^- = KNO_3(s) ; \Delta F_{25} = -92 \qquad (11)$$

whence, by combination of Equation (7) with Equation (11)

$$KCl(s) + 2NO_2(g) = KNO_3(s) + NOCl(g)$$
$$; \Delta F_{25} = -5,623 \qquad (12)$$
Since $N_2O_4 = 2NO_2$; $\Delta F_{25} = 1,127 \qquad (13)$
Also, $KCl(s) + N_2O_4(g) = KNO_3(s) + NOCl(g)$
$$; \Delta F_{25} = -4,496 \qquad (14)$$

The free energy differences of Equations (12) and (14), both being negative values of several thousand calories, indicate that potassium chloride will react with nitrogen dioxide at ordinary temperatures to form potassium nitrate and nitrosyl chloride. Futhermore, calculations of the heats of reaction, using the data of the International Critical Tables[3], give values of ΔH_{18} as $-16,691$ and $-3,683$ calories, respectively, for Equation (12) and (14) ; so the reaction should be exothermic.

III. Experimental

The general procedure consisted in passing nitrogen dioxide gas through a column packed with potassium chloride crystals and determining the nature of the products of the reaction.

The nitrogen dioxide, prepared by the oxidation of ammonia with oxygen, was supplied by Research Center of Pharmacy, Won Kwang University.

It contained some nitric oxide and probably also nitrous and nitric acids, and was purified by triple distillation. In each distillation, oxygen was bubbled through the liquid nitrogen dioxide and passed with the gaseous dioxide through a phosphorus pentoxide drying tube and then through the condenser where the nitrogen dioxide was condensed.

As showed Figure 1, liquid nitrogen dioxide, contained in a tube to which was sealed the female part of the ground joint, J, was introduced into the generator, G, by completing the joint at J and opening the stopcock on the generator and another on the nitrogen dioxide tube. The dioxide was boiled off by means of the nichrome heating element, H, and passed through the column, C, packed with slightly moist potassium chloride crystals. The gases issuing from T passed through the bulb, B, and then through a trap immersed in carbon dioxide snow (not shown) when the nitrosyl chloride was condensed. When the gas flow had continued long enough to completely flush out B and to establish a steady state throughout the entire apparatus, B was isolated and the gases allowed to pass through the by-pass connections shown, for a time sufficient to collect about 50millilitre of liquid nitrosyl chloride.

And also, as showed Figure 2, ten cubic centimeters of nitrosyl chloride were introduced into the glass cylinder, C, of about 15ml capacity, equipped with a thermocouple well,

W, of thin-walled tubing, and a glass stirrer, S, consisting of a ring sealed to one end of a rod that extended out through the side tube, T. A flexible rubber sleeve, R, permitted the operation of the stirrer without admitting air or moisture to the apparatus.

The apparatus was cooled by immersion in an acetone-carbon dioxide snow bath contained in a Dewar flask. The temperature of the bath was adjusted by adding small pieces of carbon dioxide snow. The temperature changes were followed with a carefully calibrated copper-constantan thermocouple of wire (No. 30), inserted in the well, W. The cold junction was maintained at 0℃, by an ice-water bath and the electromotive force was read with a potentiometer and galvanometer. The thermo-couple was calibrated by means of the boiling point of ammonia, and the subliming tempera-ture of carbon dioxide snow, both corrected for the barometric pressure, The ice point was taken for the third point. The potassium chloride and other reagents used were the chemically pure grade.

IV. Results and Discussion

1) Effect of moisture on the reaction

A tube, containing the purified liquid nitrogen dioxide, was sealed to the column containing potassium chloride crystals that had been dried at 110℃, and a trap for condensing the effluent gas was sealed to the outlet of the column. Dry oxygen was then passed through the reaction column and the trap for three to four hours to remove any moisture that might have gotten into the apparatus when the seals were made. Twenty-five cubic centimeters of liquid nitrogen dioxide (a large excess) were allowed to evaporate through the patassium chloride column over a period of 24 hours. The reaction column was then flushed out with dry oxygen to remove any nitrogen-containing

gases, and the nitrogen content of the salt therein was determined by the Devarda alloy method.

Although a large excess of nitrogen dioxide had been used, it was found that the salt contained only 1.6 percent of potassium nitrate on the assumption that all the nitrogen was present as nitrate.

In a second experiment the anhydrous salt was replaced by potassium chloride that contained 2.5 percent of moisture. About 20millilitre of liquid nitrogen dioxide was vaporized and allowed to pass through the potassium chloride in the course of three hours. After the column had been flushed out with oxygen to remove the nitrogen-containing gases, the salt that remained in the column had, after drying at 110℃, a nitrogen content corresponding to 92.1 percent of potassium nitrate.

Thermodynamical calculation[8-10] indicate that the formation of potassium nitrite from potassium chloride and nitrogen dioxide is very unlikely. Moreover, tests of the salt produced by the reaction showed no nitrite to be present, although good tests were obtained for nitrate.

The foregoing experiments showed that, although dry potassium chloride underwent but little change through the action of nitrogen dioxide, even after exposure of 24 hours, nearly complete conversion to potassium nitrate was accomplished in the presence of a small amount of water within three hours. As indicated later, the reaction with the moist salt was quite repid.

To determine the nature of the gaseous products of the reaction, the procedure was changed so that an excess of potassium chloride was used, and the gases escaping from the potassium chloride were sampled and examined.

The apparatus used is illustrated in Figure 1.

J : Ground joint
G : Generator
H : Nichrome heating element
C : Column
B : Bulb
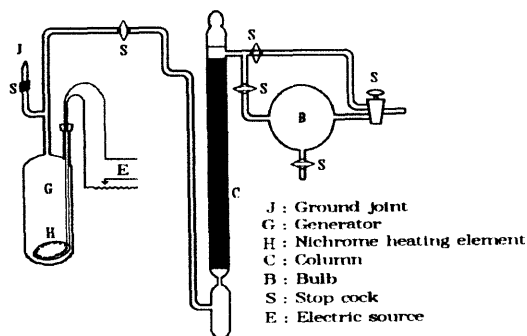S : Stop cock
E : Electric source

Figure 1. Illustration of apparatus for determining nature of gaseous reaction products.

The course of the reaction upward through the column can be followed visually by means of the reddish appearance of the salt below the advancing zone of reaction, due to the nitrogen dioxide in the interstices, and the straw-colored aspect above this zone, due to the nitrosyl chloride produced. The line of demarcation is quite distinct. The exothermic nature of the reaction is evidenced by a decided increase in the temperature of the column wall at the reaction zone. The small amount of water necessary for the reaction suggests that its function may be catalytic, perhaps by taking part in an intermediate reaction.

The contents of the bulb, B were sampled by attaching a weighed and evacuated 500millilitre gas balloon at the stopcock, S. These operations were carried out before the zone of reaction had reached the top of the column so that there would be no obvious contamination of the gaseous products with nitrogen dioxide.

The gases issuing from the potassium chloride had the characteristic claybank or amber color of nitrosyl chloride (when looking through a depth of about 10mm or less) and solidified to a light blood-red solid which melted immediately on removal from the carbon dioxide snow to a cherry-red liquid. When a portion of this condensate was allowed to evaporate, it disappeared entirely before the ice, which collected on the exterior of the trap, began to melt ; this would not have been the case had any appreciable amount of nitrogen dioxide been present.

The melting point of the nitrosyl chloride was determined, using the apparatus shown in Figure 2.

C : Glass cylinder
W : Thermocouple well
S : Glass stirrer
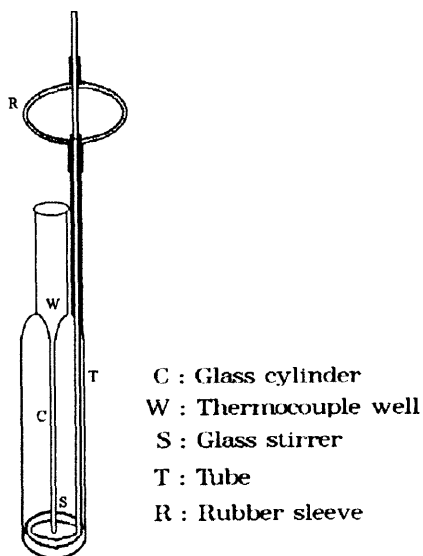T : Tube
R : Rubber sleeve

Figure 2. Schematic of apparatus for determining melting point.

The temperatures corresponding to twelve electromotive force readings, made in determining the melting point of the nitrosyl chloride, averaged −61.4℃. This is in exact agreement with the carefully determined value of Trautz et al.[11] It should be noted that this nitrosyl chloride had not been subjected to any purification but was condensed out immediately after leaving the potassium chloride column.

The gas sample in the balloon (0.5735 gram of gas) was absorbed in a known amount of 0.3 N sodium hydroxide, and the excess of sodium hydroxide was titrated with 0.5 N sulfuric acid, using phenolphthalein as an indicator. The titrated liquor was made up to

Table 1. Activity coefficients of potassium nitrate in solutions

m	$\theta(1)$	$\theta/m(1)$	$+\psi$	$\psi/2.303$	$\dfrac{\sqrt{a}}{m}$	$-\log\dfrac{\sqrt{a}}{m}$	$\dfrac{0.000125}{n}\displaystyle\int_0^m \dfrac{\theta}{m}\cdot d\theta$	$\displaystyle\int_0^m \psi\, d\log m$
0.01	0.03590	3.590	0.0338	0.01470	0.915	0.0390	—	0.0242
0.05	0.17155	3.432	0.0767	0.03330	0.806	0.0945	0.0001	0.0613
0.10	0.33140	3.314	0.1082	0.04698	0.732	0.1357	0.0001	0.0888
0.20	0.63080	3.154	0.1512	0.06565	0.642	0.1932	0.0003	0.1278
0.30	0.91440	3.048	0.1798	0.07807	0.583	0.2346	0.0004	0.1569
0.50	1.44100	2.882	0.2244	0.09748	0.503	0.2984	0.0006	0.2015
1.00	2.56000	2.559	0.3111	0.13508	0.385	0.4151	0.0010	0.2810
1.247	3.00500	2.409	0.3516	0.15261	0.344	0.4642	0.0011	0.3127

the 500millilitre, and chlorine was determined gravimetrically in a 100millilitre aliquot. Nitrogen was determined by the Devarda alloy method in another 100millilitre aliquot. Assuming that the acidity of the gas was due to nitrosyl chloride, and that the absorption in alkali took place according to the reaction

$$NOCl + 2NaOH \longrightarrow NaNO_2 + NaCl$$
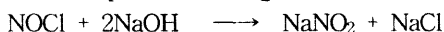
the gas contained 95.5 percent nitrosyl chloride by weight. The remaining 4.5 percent may be accounted for by permanent gases (chiefly air) in the sample.

The chlorine determinations, when calculated to nitrosyl chloride, accounted for 97.1 percent of the titratable gas in the sample when the latter was calculated to nitrosyl chloride. The nitrogen determinations. calculated in the same way, accounted for 97.2 percent. The agreement was so good as to leave little doubt that the gas was principally nitrosyl chloride.

The foregoing data are representative of those from several experiments, only one of which is given because of small deviations in procedure which rendered the others not strictly comparable. The other experiments, however, bear out in every way the conclusions reached in this paper.[12,13]

2) Velocity of the Reaction

The decided increase in temperature of the column at the reaction zone is evidence of a rapid reaction, since otherwise the heat of reaction would have been conducted away before any appreciable rise in temperature occurred. Moreover, the only visible effect of changing the rate of flow of nitrogen dioxide over rather wide limits (e. g., by doubling or tripling the amount of current passed through the heater used to vaporize the peroxide) was to cause the reaction zone to proceed more rapidly up the column. At no time was nitrogen dioxide observed escaping from the column before the reaction zone reached the top. Copious red fumes of nitrogen dioxide did appear, however, the moment that the upper edge of the reaction zone reached the top of the potassium chloride in the column.

In fact, the main concern in most of the experiments was to prevent the reaction zone from reaching the top of the potassium chloride column too rapidly.

Otherwise the gaseous reaction products would have been mixed with nitrogen dioxide, thus interfering with their determination.

It was found, however, that further conversion occurs after the reaction zone proper has passed on. Thus the nitrate content of the converted salt was always higher at the bottom of the column than at the top.

In a typical case, in which the flow of nitrogen dioxide was stopped when the reaction zone reached the top of the salt column, the salt from the upper part was 43 percent potassium nitrate, as calculated from its nitrogen content, while that from the lower part was 82 percent nitrate. That no intermediate products were produced was evident from an analysis of the 43 percent potassium nitrate material which showed no other salt but potassium chloride present.

The most complete conversion was obtained by continuing the nitrogen dioxide flow for a time after the reaction zone had disappeared. This was done in the experiment described in which the treated salt contained 92 percent potassium nitrate.

This delay in conversion is probably not due to slowness of the reaction but to the time required for the nitrogen dioxide to penetrate to the interior of the potassium chloride crystals.

Conclusion

The process of preparing potassium nitrate from potassium chloride and nitrogen dioxide becomes a cyclic one when operated in connection with a plant for the absorption of nitrogen dioxide.

Thermodynamical calculations indicate that the formation of potassium nitrite from potassium chloride and nitrogen dioxide is very unlikely. The tests of the salt produced by the reaction showed no nitrite to be present, although good tests were obtained for nitrate.

Nearly complete conversion to potassium nitrate was accomplished in the presence of a small amount of water within three hours. While that no intermediate products were produced was evident from an analysis of the forty-five percent potassium nitrate material which showed no other salt but potassium chloride present. The most complete conversion was obtained by continuing the nitrogen dioxide flow for a time after the reaction zone had disappeared. Nitrosyl chloride is produced simultaneously.

Nomenclatures

s : solid state

g : gaseous state

a : activity of solute

m : molality

n : number of ions formed

θ : freezing point lowering

λ : molal freezing point lowering at infinite dilution by non-dissociating molecule (= 1.858)

ϕ : $1 - \theta / nm \lambda$

ΔF : free energy change

ΔH : enthalpy change

T : temperature

ΔC_P : specific heat change at constant pressure.

R : gas constant

Acknowledgements

References

1. Jones, U. S., "Fertilizers and Soil Fertility", 2nd ed., Prentice-Hall, Inc., 1982.

2. Mehring, A. L., Ross, W. H., and Merz, A. R., *Ind. Eng. Chem.*, 21, 379(1929).

3. International Critical Tables, Vol. IV-VII, McGraw-Hill Book Co., New York, 1926.

4. Lewis, G. N. and Randall, H., "Thermodynamics", McGraw-Hill Book Co., New York, 1923.

5. Lewis, G. N. and Randall, M., 2nd ed., revised by Pitzer, K. S. and Brewer, L., "Thermodynamics", McGraw-Hill Book Co., New York, 1961.

6. Randall, M. and Rossini, *J. Am. Chem. Soc.*, 51, 335 (1929).

7. Dodge, B. F., "Chemical Engineering Thermo dynamics", McGraw-Hill Book Co., New York, 1944.

8. Reynolds, W. C., "Thermodynamics", 2nd ed., McGraw-Hill Book Co., New York, 1968.

9. Hougen, O. A., Watson, K. M., and Ragatz, R. A., "Chemical Process Principles", Part II, "Thermodynamics", 2nd ed., John Wiley & Sons, Inc., New York, 1959.

10. Perry. R. H. and Chilton, C. H., "Chemical Engineer's Handbook", 5th ed., McGraw-Hill Book Co., Kogakusha, 1973.

11. Trautz, and Gerwig., *Z. anorg. allgem. Chem.*, 134, 409 (1924).

12. Sauchell, V. (ed.), "Chemistry and Technology of Fertilizers", ACS Monograph 148, Reinhold, New York, 1960.

13. Noyes, R., "Potash and Potassium Fertilizers", Noyes, Park Ridge, N. J., 1966.