THE SEPARATION OF STABLE NITROGEN ISOTOPES

BY THE CHEMICAL EXCHANGE METHOD, II

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We have previously recorded $\diagup$ 1 $\diagup$ that during the
separation of isotopes by the chemical exchange method
according to the reaction:

$$N^{15}H_{3(r)} + N^{14}H_4NO_{3(p)} \rightleftarrows N^{14}H_{3(r)} + N^{15}H_4NO_{3(p)}, \qquad (1)$$
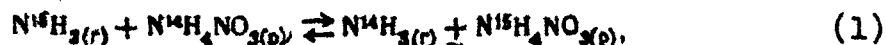
an important part is played, together with the nature of
the packing, by its external surface determined by the
geometrical dimensions of the separate elements of the
packing. It was pointed out that the separation of iso-
topes improves with the drop of the partial pressure of
ammonia gas in the column. In addition to this it was
pointed out that simultaneously with the decrease of par-
tial pressure of ammonia gas by the introduction of nitro-
gen - there occurs an increase in the lineal rate of flow
of ammonia into the system. A supposition was expressed
that the increase in the rate of flow apparently also
influences the effectiveness of the separation of the
isotopes.
    The question of the influence of the rate of flow
of components in the exchange reaction (1) on the separa-
tion of nitrogen isotopes, judging by the published data,
has not been sufficiently investigated. There are des-
criptions of results of some of the unsystematic experi-
ments by Urey, Hoffman, Thode and Fox $\diagup$ 2 $\diagup$ conducted
with various rates of admission of the solution, from
which it is impossible to draw a well-defined conclusion
concerning the role played by the rate of flow during the

chemical separation of the nitrogen isotopes.

A definite effect on the separation of isotopes is exerted by the temperature at which the process of separation takes place. An increase in the temperature leads on the one hand to the decrease of the constant of the equilibrium of the reaction (1) and on the other hand leads toward decrease of solubility of the ammonia gas in the solution of ammonia nitrate and of the constant of the equilibrium of the reaction:

$$N^{15}H_{3(r)} \pm N^{14}H_{3(p)} \rightleftarrows N^{14}H_{3(r)} + N^{15}H_{3(p)}, \tag{2}$$

taking place simultaneously with the first reaction. If the first effect will result in the decrease of the coefficient of a single-stage separation, the last two on the contrary will result in the increase of this coefficient. Owing to this it is possible to expect the presence of an optimum temperature in the process under consideration. There are few facts published in connection with the problem. In work $\sqrt{2\_\!/}$ it was shown that the coefficient of separation observed at room temperature is higher than at 60° C. Nakane $\sqrt{3\_\!/}$ arrived at the conclusion that the optimum temperature is 10° C.

The problem of this work is to clarify the relationship between the separation of isotopes of nitrogen and the rate of flow of reagents and the temperature in the column.

The effect of rate of flow. The investigation was conducted in an installation previously described, in which only the length of the column was changed (to 220 cm.). The separation of isotopes was accomplished with a packing of passivated nichrome wire prepared in the shape of small trihedral prisms of 3 mm. The intake rate of the nitrate of ammonia solution was varied from 2 to 8 ml/min. The temperature of water delivered to the external jacket of the column was varied from 20 to 80° C. The total pressure in the system (this pressure is equal to the sum of the pressure of ammonia and steam) was 1 atmosphere. Figures 1 - 3 show kinetic curves of the separation of isotopes of nitrogen obtained for three intake speeds of the salt solution: 2, 5 and 8 ml/min. Each speed was investigated at 20°, 40°, and 80° C.
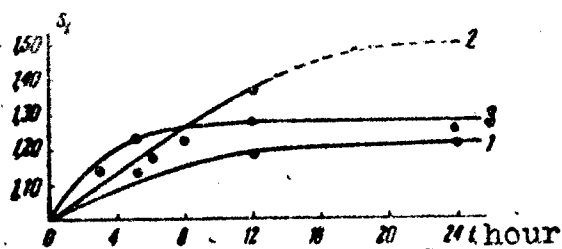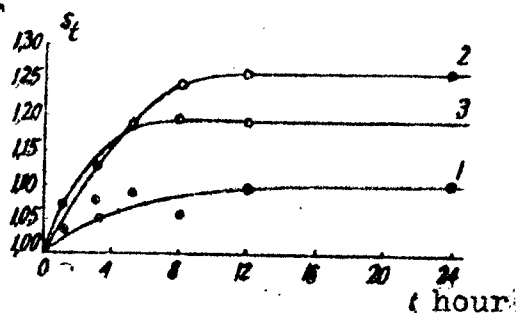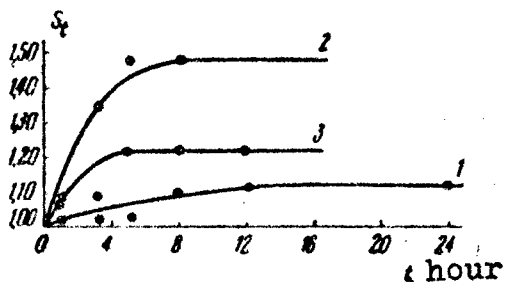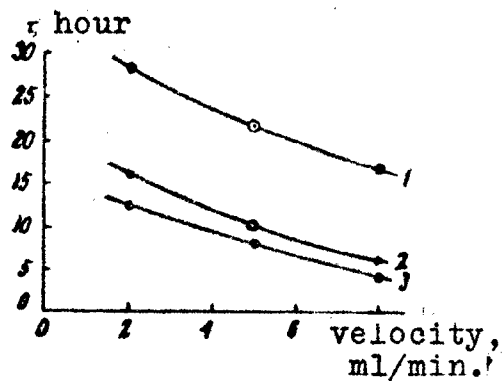
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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 1. Relationship between the coefficient of enrichment and the time, at 20° C. and various rates of solution intake: 1 - 2 ml/min.; 2 - 5 ml/min.; 3 - 8 ml/min.

Fig. 2. Relationship between the general coefficient of enrichment and the time at 40° C. and at various rates of the solution intake. The designations are the same as in Fig. 1.

Fig. 3. Relationship between the general coefficient of enrichment and the time at 80° C. and at various rates of solution intake. The designations are the same as for Fig. 1.

Fig. 4. Relationship between the time required to reach a stable condition and the solution intake rate, with the column at different temperatures: 1 - 20°; 2 - 40°; 3 - 80° C. The point, encircled with dotted lines, was arrived at by extrapolation.

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An analysis of the kinetic curves indicates that the greatest enrichment at all temperatures (under the conditions of our experiment) was obtained at an intake rate of the solution at 5 ml/min. During this time the attainment of the stationary state was decreasing correspondingly with the increase of the intake rate of the solution (Fig. 4). We were not successful in conducting experiments at a greater rate with the utilized packing because at the rate of 10 ml/min. the column became flooded. This can be explained by the great speed of the flow of the forming ammonia gas (100 l/hours or 11 cm/sec.) which offered great resistance to the salt solution flow. At intake rates of the solution less than 2 ml/min., it was difficult to regulate its constancy in relation to time. Isotope analysis of the samples, taken at different times from the liquid phase in this case, would be a subject of great fluctuation, because of the short duration of fluctuations /_4_/ in particular because of the fluctuation of the flow rate.

Effect of Temperature. The study of the effect of temperature on the separation of nitrogen isotopes was conducted in the interval of temperatures from 10 to 80° C. with the intake rate of the solution at 2 ml/min. and in the interval of 20 - 80°, with corresponding rates of 5 and 8 ml/min. We obtained five kinetic curves (Fig. 5) for rates 2 ml/min. (one curve each at 10°, 20°, 40°, 60° and 80°) and three curves for rates 5 and 8 ml/min. (at 20°, 40° and 80°, Figs. 6, 7). As is apparent from the figures, the greatest enrichment in our experiment was reached at 20°. With the increase of the temperature up to 40° the enrichment diminishes during all intake rates studied by us, but above 40° it starts increasing. As a result of this, with solution intake rates of 5 and 8 ml/min. and temperatures of 80° the value of balanced common coefficients of separation becomes almost equal to the corresponding values for 20°. The relationship observed by us can be explained, apparently, by a compensation of two factors causing a contrasting influence during the increase of the temperature on the value of the coefficient of separation. This decrease of the equilibrium constant in the equation of isotope exchange (1), leads to the decrease of the coefficient of a single-stage

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separation, on the one hand, and to the reduction of the
height of the theoretical plate due to the increase of
the exchange rate on the other hand. From the spectro-
scopic data we calculated the equilibrium constant of
the reation.

$$N^{15}H_{3(r)} + N^{14}H^+_{4(p)} \rightleftarrows N^{14}H_{3(r)} + N^{15}H^+_{4(p)}. \tag{3}$$
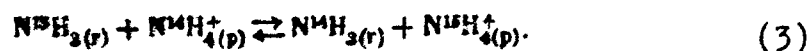
For 10°, 20°, 40°, and 60° the corresponding values for
K were 1.0369; 1.035; 1.032 and 1.030. The value for K
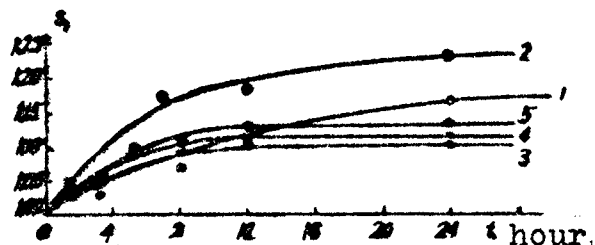for 80° obtained by extrapolation was equal to 1.028.

Fig. 5.   Relationship between the general coeffi-
cient of enrichment and the time at
V = 2 ml/min. and at various temperatures:
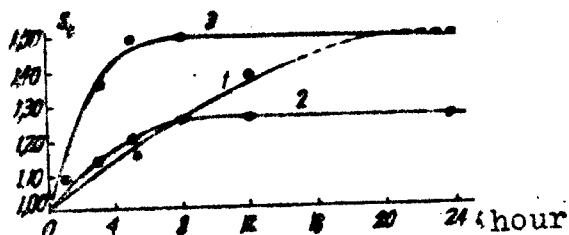1 – 10°; 2 – 20°; 3 – 40°; 4 – 60° and
5 – 80° C.

Fig. 6.   Relationship between the general coeffi-
cient of enrichment and the time at V =
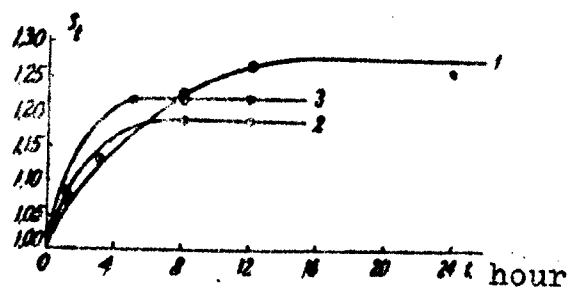ml/min. and various temperatures: 1 – 20°;
2 – 40°; and 3 – 80° C.

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Fig. 7. Relationship between the general coeffi-
cient of enrichment and the time at
V = 8 ml/min. and various temperatures:
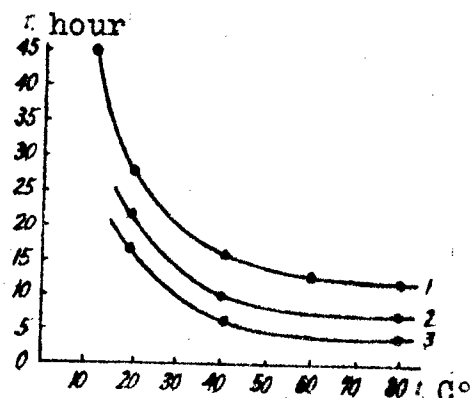1- 20°; 2 - 40° and 3 - 80° C.

Fig. 8. Relationship between the time required for
a stationary state and the time at various
speeds of solution intake into the column:
1 - 2 ml/min. 2 - 5 ml/min; 3 - 8 ml/min.
The point encircled with dotted lines was
arrived at by extrapolation.

On the other hand, with the increase of the tempe-
rature the constant K' of the exchange reaction (2) also
decreases, as does the solubility of ammonia gas in the
solution of salts. According to the half-empiric formula:

$$\alpha = K - (K - K') M,\qquad\qquad(4)$$

submitted by Kirshbaum and his coworkers $\underline{/5\underline{/}}$ this leads
to the increase of the coefficient of a single-stage

separation. Here K and K' are constants of the equilibrium of the exchange reactions (3) and (2), and M is a molar part of the dissolved ammonia gas in the solution, equal to:

$$M = \frac{[NH_3]_p}{[NH_3]_p + [NH_4^+]_p} . \qquad (5)$$

We made no attempt to determine the molar part of dissolved ammonia gas in the solution of ammonia nitrate under the working conditions of our installation, but from the published data $\underline{/\,6\,\underline{/}}$ it is known that in the balanced conditions this part differs little from the solutiblity of ammonia gas in water. Because of this, and on the basis of indirect data on the sharp decrease of the solubility of ammonia gas in aqueous solution with the increase of the temperature, it is possible to admit as a proved supposition that there is some compensation for α in Formula (4) because of the diminishment of M. It is apparent from Fig. (5) that the value of the common coefficient of enrichment at 10° C. through the entire length of the curve (up to the state of equilibrium which occurs after 44 hours) is smaller than corresponding values at 20°. This fact can be partially explained by reduction in the speed of the solubility of ammonium nitrate, which under equal conditions leads to reduction of the coefficient of a single-stage separation (2). Owing to a lessening of the solubility of ammonium nitrate we were forced to use a 50% solution at 10° whereas in all other experiments we used a 60% solution of NH_4NO_3. The relationship between the time necessary for reaching a stationary state and the temperature is shown in Fig. 8. The curves indicate that at all speeds and temperatures investigated by us, the value of this time diminishes with the increase of the temperature.

Conclusions

1. The effect of the rate of flow and the temperature on the separation of nitrogen isotopes was investigated in a column with a packing under the conditions of counterflow.

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2. It was shown that the time for reaching a stationary state diminishes with the increase on the rate of the flow and the temperature.

3. It was discovered that under the conditions of our work there exists an optimum rate of flow (the input of the solution and, correspondingly, the return of ammonia into the column) at which the greatest separation of the nitrogen isotopes occurs.

4. It was found that the common coefficient of the separation of isotopes diminishes with the increase of the temperature from 20 to 40 (at all flow rates investigated by us), and afterward increases proportionately to the increase of the temperature. Such a relation can be explained by the change of the coefficient of enrichment, because of the simultaneous change of the temperature constant of the balance of the exchange reactions, taking place in the column and also by the speed of the exchange and the molar part of the dissolved ammonia gas.

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