

In conclusion, let us note that the theory that has been developed is correct so long as

$$R, H \gg \lambda_* = \lambda \left\{ 1 + \frac{p_0'}{\lambda_0 \sqrt{\rho_{00} a_{00}}} \int_{t_0}^t \left[\frac{m_0}{\sqrt{\rho_0 a_0}} \frac{1}{L} \times \exp \left(\int_{t_0}^{\tau} v_{0i} n_i \frac{\partial n_i}{\partial x_i} d\tau' \right) \right] d\tau \right\}^{1/2}$$

is fulfilled, which can restrict the limits of its application when $l \rightarrow \infty$. In the case when $H \gg \lambda_*$, Eqs. (2.4) and (2.5) have an asymptotic nature.

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Reaction of Producing Hydrogen Peroxide in Liquid Ammonia

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THE study of reactions of peroxide compounds in liquid ammonia is particularly interesting. Peroxides in this solvent were first obtained by the action of dry oxygen on solutions of alkaline metals¹ and alkaline earth metals.² Afterward these reactions were studied in detail.³⁻⁹ The reactions of the double exchange between suspensions of hyperoxides of sodium and potassium and solutions of nitrates of various metals were investigated.⁹⁻¹¹ In the separation of inorganic ozonides, ammonia was used as a dissolvent.^{12, 13} References to the study of reactions between hydrogen peroxide and alkaline metals or their derivatives in a solution of liquid ammonia were not found in the literature.

At temperatures below -30° and concentration of more than 35% by weight, hydrogen peroxide forms sufficiently stable solutions in liquid ammonia.¹⁴ In water solution the dissociation K of H_2O_2 after the first stage is equal to $\sim 1 \times 10^{-12}$. In liquid ammonia it should increase, since affinity for the proton of the molecule of this solvent is greater than for the molecule of water. Alkaline metals, their amides, and a number of salts, such as nitrates, nitrites, perchlorates, rhodonides, and others, form stable solutions in liquid ammonia. We undertook a thermodynamic evaluation of the possibility of reactions between hydrogen peroxide and the enumerated classes of compounds (metal, amide, salt of oxygen acid) in liquid ammonia. As an example sodium and its derivatives were chosen.

Standard thermodynamic data for the substances participating in the reaction were taken from literature,¹⁵⁻¹⁹ S° data for $NaNH_2$ (solid) and NH_3 (liquid) were not found. The

absence of S° values for any amides does not permit us to estimate this quantity for $NaNH_2$; $S^\circ NH_3$ (liquid) was assumed equal to 28 cal/deg-mole, taking into account changes of S° for H_2O and H_2O_2 as a function of ΔH° at the transition from liquid into the gaseous state. Results of the calculation are given in Table 1.

The displacement of hydrogen from H_2O_2 by metallic sodium according to reaction 1 ought to be no less successful in ammonia than in ether.²⁰ The interaction of amide with H_2O_2 by reaction 2, corresponding to the process of neutralization in water solution, ought to proceed in the direction of creating sodium peroxide. This is confirmed by the substantially larger negative ΔH° value of the reaction, which will hardly permit us to obtain a positive ΔZ° value after accounting for the entropic term.

Judging by the magnitude of ΔZ° , reaction 3 in liquid ammonia ought to proceed from right to left, that is, an accumulation of hydrogen peroxide will take place. Calculation of the magnitude ΔZ° of the reaction 3 for the temperature range -50° to $+100^\circ C$ gives for -50° the value $+6$ kcal/mole and for 100° the value $+22.4$ kcal/mole. The preserva-

Table 1 Evaluation of the possibility of producing hydrogen peroxide reactions in liquid ammonia

Reaction	ΔH° , kcal/ mole	S° , kcal/ deg- mole	ΔZ° , kcal/ mole
1) $2Na(s) + H_2O_2(l) = Na_2O_2(s) + H_2(g)$	-85.8	+7.4	-83.6
2) $2NaNH_2(s) + H_2O_2(l) = Na_2O_2(s) + 2NH_3(g)$	-53.0
3) $2NaNH_2(s) + H_2O_2(l) = Na_2O_2(s) + 2NH_4NO_3(s)$	+6.6	-39.0	+18.2

Translated from *Izvestiia Sibirskogo Otdelenie Akademii Nauk SSSR* (Bulletin of the Siberian Branch of the Academy of Sciences USSR), no. 11, 130-132 (1961). Translated by Nathan Harlap, Berkley, Calif.

tion of a positive value for ΔZ confirms that ΔZ° data may be used as an inference on the possibility of a reaction at the temperature of liquid ammonia.²¹ Experimental checking confirmed the correctness of such a conclusion.*

As a medium for the reaction, liquid synthetic ammonia was used.²² To remove the moisture, the ammonia condensed itself on metallic sodium after entering the reactor. The sodium peroxide used in the experiments contained no water. Its composition was 93.12% Na_2O_2 , 2.26% Na_2CO_3 , and 4.93% NaOH . Ammonium nitrate (technical) was purified by the known method,²³ and after drying on filter paper, it contained 1.6% H_2O (determined by the method of Fisher).

To accomplish the reaction, a weighted amount of sodium peroxide was introduced into a reactor of 100 ml capacity. The reactor was placed in a Dewar flask with a mixture of dry carbonic acid and ethyl alcohol at a temperature of -50 to -60° ; after cooling, the liquid ammonia was introduced into it, and the apparatus was shaken for half an hour. After it settled, samples of the liquid were taken with a dry pipette, which was cooled beforehand, into a vial of water containing sulfuric acid with a Congo red indicator. The indicator is used to prevent the introduction of an excess of ammonia (in relation to the sulfuric acid) into the vial with the liquid sample—in alkaline water solution peroxide decomposes rapidly. Titration of the obtained solution with a permanganate showed the absence of peroxide ion in the solution. This confirms the fact that the sodium peroxide is not soluble in liquid ammonia. Next, ammonium nitrate in molar relation with Na_2O_2 , according to the equation of reaction 3, was added in the reactor, after which the solution was shaken another half hour. The sodium peroxide was not completely dissolved. In the sample of the liquid phase taken after the solution settled the content of oxygen peroxide corresponded to the concentration of 1.5% H_2O_2 .

In the second experiment, Na_2O_2 and NH_4NO_3 were used in molar relation 2:1. In this case the content of active oxygen, calculated in relation to H_2O_2 , was as follows: in 25 min—0.6%; in 35 min—1.5%; in 55 min—2.1%; in 85 min—2.0%. As can be seen, an equilibrium is established in the solution, and the concentration of oxygen peroxide becomes a constant. By our estimate, approximately 80% of the sodium peroxide was transformed into hydrogen peroxide.

* Calculation of reaction 3 for the temperature range was by the formula $\Delta Z_m = -RT_m \ln K_{pm}$; change in thermal capacity was disregarded, and it was assumed that H_2O_2 (gaseous) and NH_3 (gaseous) participated in the reaction.

The data obtained show the possibility of bringing about an exchange reaction between solid sodium peroxide and ammonium nitrate dissolved in liquid ammonia. In such a reaction, ammonium nitrate (monoammoniate HNO_3) acts like an acid; that is, its action is analogous to the action of acid hydrate on an Na_2O_2 sediment in a water medium.

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