Fractions 6 and 7 were analysed by the dinitrofluorobenzene method following mainly Schroeder's instructions. The chromatography of DNP-compounds was, however, made according to Blackburn and Lowther [5]. The non-terminal amino acids were also converted to DNP-compounds and chromatographed. DNP-proline was identified additionally by the spectrum. All the DNP-amino acids were chromatographed with mixed crystallised references.

The following results could be obtained for peptides eluted at pH 3.42. (The asterisk indicates comparatively small amount.)

Fraction 6, peptide 1*: Glu-(Asp, Gly, Val*, Leu *)
peptide 2: Pro-(Asp, Glu, Gly, Val *, Leu*);

this peptide may be contaminated with another with valine as N-terminal amino acid.

Fraction 7, peptide 1: Gly-(Asp, Glu, Val*, Leu*, Gly?)
peptide 2: Ala-(Asp, Glu, Gly, Val*, Ala?)
peptide 3*: Val-(Asp, Glu, Gly, Ala, Pro)

The remarkable point is the abundance of aspartic and glutamic acids, which are present in small amounts in elastin, and the peptide breaks easily at aspartic acid. Common constituents are in these peptides Asp, Glu, Gly and in traces Val. Further investigation will show whether they form a characteristic sequence. In gelatin this region (pH 3.42) contains only two peptides Ala-Asp and Gly-Asp in quite small amounts, while proline and glycine peptides form the main part of the hydrolysate[2].

The form of the fractionation curve or the composition of the peptides which emerge at pH 3.42 do not support the concept of conversion of collagen to elastin at peptide level.

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# Diamagnetism of LiNO, NaNO and KNO

## Studies in Magnetochemistry 19 *

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The direct reaction between sodium metal and nitric oxide results in a reduction of nitric oxide. If, however, the process is carried out in liquid ammonia the result of the reaction is the formation of sodium nitrosyl (NaNO). Joannis [1], who first studied this reaction, prepared the sodium and potassium compounds and considered these substances as hyponitrites. Zintl and Harder [2] reprepared the sodium nitrosyl. Frazer and Long [3] measured the magnetic susceptibility of sodium nitrosyl and state that the compound is diamagnetic but give no numerical value.

The alkali metal nitrosyls are colourless or nearly colourless crystalpowders. The X-ray powder photo of the sodium compound is different from that of anhydrous sodium hyponitrite. The lines are very diffuse, an indexing could not be carried out (cf. also Zintl and Harder [2]). The aqueous solution is not stable; also at 0°C the solution is decomposed under evolution of nitrous oxide. Under corresponding conditions a sodium hyponitrite solution is stable or decomposes very slowly. These facts indicate that the compounds are not $hypo_n$ nitrites but may be considered as $(NaNO)_n$ and $(KNO)_n$. We may propose the ionic structures

$$\overset{+}{Na}(N\overline{O}) \text{ and } \overset{+}{K}(N\overline{O}).$$

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Since $N\bar{O}$ and $O_2$ are isosteres it is possible that the ground state of the $N\bar{O}$-ion is a triplet state. This state gives a magnetic moment $\mu = 2.83\ \mu_B$. In order to settle this question the metal nitrosyls LiNO, NaNO and KNO were prepared and measured magnetically; LiNO was prepared for the first time. The results of the chemical analyses and the magnetic measurements are given in Table 1. The results prove that $N\bar{O}$ is in a singlet state — if present in these compounds.

*Table 1.* Analyses and diamagnetic susceptibilities of alkali metal nitrosyls.

| Substance | % Metal calc. | % Metal found | $\chi_g \times 10^6$ | $\chi_M \times 10^6$ | $\chi_{N\bar{O}} \times 10^6$ |
|---|---|---|---|---|---|
| LiNO | 18.78 | 18.50 | $-0.56_2$ | −20.8 | −20.1 |
| NaNO | 43.37 | 42.98 | $-0.40_0$ | −21.2 | −17.2 |
| KNO | 56.57 | 56.42 | $-0.46_4$ | −32.1 | −18.1 |

The metals were determined as sulphates. The metal nitrosyls were measured magnetically in evacuated glass tubes (Gouy method) at 20—22°C.

The gram ionic susceptibilities for $NO^-$ were calculated from the $\chi_M$ values by means of the gram ionic susceptibilities $-0.7 \times 10^{-6}$, $-4 \times 10^{-6}$ and $-14 \times 10^{-6}$ for the ions $Li^+$, $Na^+$ and $K^+$, respectively. *A reasonable mean value for the gram ionic susceptibility of* $NO^-$ *is* $-18 \times 10^{-6}$. This number is calculated from the 3 values in Table 1 giving the values for NaNO and KNO double weight because the analytical data for these substances are in better accordance with the theoretical values than is the case for LiNO.

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# On the Existence of Oscillating Enzymatic Reactions and on a Possible Interpretation of Spontaneous Spike Potentials in Nerves

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An overall reaction

$$A_1 + A_2 + A_3 \rightleftharpoons B_2 + B_3 + B_1 \qquad (B)$$

is supposed to be catalyzed by an enzyme according to the mechanism (A)

$$\begin{aligned} A_1 + X_1 &\rightleftharpoons X_2 + B_2 \quad (\pm 1) \\ A_2 + X_2 &\rightleftharpoons X_3 + B_3 \quad (\pm 2) \\ A_3 + X_3 &\rightleftharpoons X_1 + B_1 \quad (\pm 3) \end{aligned} \qquad (A)$$

where $X_1$, $X_2$, $X_3$ are three different forms of the enzyme or complexes thereof with the substrates ($A_i$, $B_i$). The sum of the concentrations of the three forms is the total constant enzyme concentration $E$, which is supposed to be stoichiometrically small as compared to the concentrations of the substrates. Let $x_1$, $x_2$ and $x_3$ be the fractions of the enzyme present in the three states, and let $s_1$, $s_2$ and $s_3$ be the resulting rates of the three partial reactions, divided by $E$.

We then have the four equations

$$\begin{aligned} x_1 w_1 - x_2 w_{-2} &= s_1 \\ x_2 w_2 - x_3 w_{-3} &= s_1 \\ x_3 w_3 - x_1 w_{-1} &= s_2 \end{aligned} \qquad (1)$$

$$x_1 + x_2 + x_3 = 1 \qquad (2)$$

where $w_1$ is the probability in unit time for $X_1$ to react according to $(+1)$ in (A), $w_{-1}$ the probability for $X_2$ to react with $B_2$ according to $(-1)$ in (A), *etc.*

The steady state solution of the system (1) in connection with the condition (2) is well known [12]. It is characteristic for this, that if the probabilities $w$ are exactly known the result of the calculation is of unlimited accuracy.

There exists, however, another solution of (1) and (2) for which this is not true in so far as in this case the (weighted) sums of the squared deviations from mean values have well defined constant values, different from zero.

This solution seems therefore to be inherently more probable than the usual one.