

let t_1 denote a complete lifetime in n , and t_2 the further lifetime from an arbitrary instant at which the state is n . It is stressed that only a relation for *mean* times has been deduced above, though it is remarkable that by a simple extension of Smoluchowski's arguments we may obtain at least one relation between the complete distributions of θ_1 and θ_2 . This is

$$\Theta_1 \Pi(z; \theta_2) = z(1 - \Pi(z; \theta_1)) / (1 - z) \quad (1)$$

for discrete time, or

$$\varphi_{\Theta_1} M(\varphi; \theta_2) = M(\varphi; \theta_1) - 1 \quad (2)$$

for continuous time, where $\Pi(z)$ denotes a probability-generating function and $M(\varphi)$ a moment-generating function. Similar relations hold between t_1 and t_2 . However, for *any* Markoff process the lifetime in state n does not depend on the history prior to the last instant, and t_1 and t_2 are in that case stochastically equivalent; the relation similar to (2) then leads to the familiar exponential distribution for t_1 or t_2 . Conversely, from (2), except under conditions for which θ_1 and θ_2 (or t_1 and t_2) become stochastically equivalent, the exponential distribution *cannot* hold exactly.

It thus still remains to determine their distributions. One possible method available for Markoff processes is to modify the standard matrix representation of the transition probabilities; this matrix, operating on any vector representing the initial probability distribution of states, generates the succeeding distributions. If we modify the matrix by prohibiting transitions *from* state n , we eliminate from all 'not n ' at any instant all 'paths' which at any time previously moved into state n , and hence we obtain any required information on times of recurrence (which are lifetimes in 'not n '). The distinction between θ_1 and θ_2 is obtained by appropriate choice of the initial vector, though from (1) or (2) only one distribution need be found.

(Note added in proof, April 27. A somewhat more general method based on renewal theory has recently been indicated by Feller³. However, as the definition of recurrence time is different, some adaptation is necessary, and the method above seems the more convenient in the present context; it readily gives, for example, the general distributional form, or the explicit condition for the exponential distribution.)

Further investigation of these distributions is being undertaken in collaboration with Mr. B. J. Prendiville.

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¹ Chandrasekhar, S., *Rev. Mod. Phys.*, **15**, 1 (1943).

² Smoluchowski, M. v., *Wien. Ber.*, **124**, 339 (1915).

³ Feller, W., *Trans. Amer. Math. Soc.*, **67**, 98 (1949).

Role of Hydrogen Molecule Ions in Aqueous Solutions

THE hydrogen molecule ion H_2^+ has played a important part in theoretical chemistry, and its existence in the gaseous phase is well established. Some of our recent experimental work on the reactions of hydrogen atoms in aqueous solutions seems to suggest that a somewhat similar ion exists also in the aqueous phase, where one may have the equilibrium:



One might be inclined to assume that this equilibrium is shifted very far towards the dissociation side because of the large heat of hydration of the proton. This, however, will be counteracted to some extent by the bond energy (2.65 eV.) of the H_2^+ molecule and also if this ion possesses a heat of hydration of considerable magnitude (its hydrated form is then perhaps better represented by $H_4O^+.aq$, similar to $H_3O^+.aq$).

From the chemical point of view the interest lies in the fact that, whereas hydrogen atoms themselves are strong reducing agents (electron donors), a hydrogen atom combined with a hydrogen ion should act as electron acceptor and exhibit oxidizing properties according to:



leading to the formation of molecular hydrogen, as, for example, the simple electron transfer processes:



We have studied a number of aqueous systems at different pH in the presence of hydrogen atoms which were produced either by ordinary (thermal) reactions or photochemically (for example, by the irradiation of certain simple ions in the near ultraviolet¹) or by the action of ionizing radiations (X-rays, γ -rays, etc.) on water², and reactions of the type discussed above appear to be of significance, particularly at lower pH values.

A full account will be published elsewhere.

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¹ Cf. Weiss, J., *Trans. Farad. Soc.*, **37**, 463 (1941).

² Cf. Weiss, J., *Nature*, **153**, 748 (1944).

Steric Inhibition of Resonance in some Organic Copper Compounds

COPPER diphenylacetate is insoluble in benzene and practically so in ethyl alcohol, but is readily soluble in a mixture of these solvents due to the formation of a compound with two molecules of alcohol¹. Similar behaviour is now found in the copper salts listed in Table 1. Copper *o*-iodobenzoate, for example, crystallizes with one molecule of alcohol.

Table 1

Solubilities (gm./100 ml.) of copper salts in benzene containing 10 per cent ethyl alcohol at 25° C.

Phenylacetate	2.73	Butyrate	18.3
Diphenylacetate	7.65	<i>o</i> -Toluate	5.58
Triphenylacetate	r.s.	<i>o</i> -Chlorobenzoate	r.s.
Hydrocinamate	r.s.	<i>o</i> -Bromobenzoate	r.s.
Propionate	7.64	<i>o</i> -Iodobenzoate	r.s.

Table 2

Benzoate	0.13	<i>p</i> -Toluate	0.01
Ginnamate	0.44	<i>p</i> -Chlorobenzoate	i.
Crotonate	0.31	<i>p</i> -Iodobenzoate	i.

r.s. = readily soluble; i. = insoluble.

Table 2 lists copper salts found to be insoluble or nearly so in the mixed solvents. It is noted that in these the carboxyl group is conjugated with a double bond in the $\alpha\beta$ -position. This will facilitate stabilization of the ion by resonance as in (I). Such ionic