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the adsorption energy and, thereby, to the longevity in the adsorbed state. This would diminish α even more pronouncedly, were it not for the rapid decrease of the saturation pressure. Therefore, it is not surprising that α -values close to unity have been found for Hg. On the other hand, almost as high values, reported for CCl_4 at temperatures very near the critical film temperature,^{6,8} are hard to reconcile with the simple picture here presented.

The preceding considerations are restricted to liquids, not because the free mobility of adatoms is insufficient on the surface of crystals, but because the structure of the crystalline surface permits of substrate-film transitions only at certain active centers, i.e. at the "half-crystal" sites of Stranski.² Primarily by this reason, surface diffusion, as another rate-determining step, has to be taken into account in the kinetics of sublimation.

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Calculations of the Lower Excited Levels of Benzene

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IN a 1938 paper under the above title,¹ Goeppert-Mayer and Sklar employed the method of antisymmetrized products of molecular orbitals to calculate the lower excited electronic energy levels of the benzene molecule. Using no other empirical data than the carbon-carbon distance, and considering the six π -electrons alone, they obtained excitation energies which agreed fairly well with experiment² (see second and last columns in Table I). It was noticed later by London,³ and independently by Goeppert-Mayer and McCallum,⁴ however, that repetition of the calculation including the small, but numerous, initially neglected terms yields results which are less encouraging (see third column in Table I).

Recently it has been found that Goeppert-Mayer and Sklar (and London) used incorrect values for certain integrals.⁵ We wish to call attention to the results that are obtained when correction is made for this. When the Goeppert-Mayer-Sklar work is re-

TABLE I. Electronic energy levels of benzene (ev).

Level	Goeppert-Mayer Sklar ¹ (I, N) ^a	London ³ (I) ^a	Craig Parr ⁵ (N) ^a	Roothaan Parr ⁴	Observed ²
¹ E _{1u} (¹ Γ ₁₂)	8.0	11.1	6.7	9.7	7.0
¹ B _{1u} (¹ Γ ₁₀)	5.8	8.8	4.2	7.2	6.2
¹ B _{2u} (¹ Γ ₉)	5.0	7.3	3.7	5.8	4.9
³ B _{2u} (³ Γ ₁₀)	3.0	7.2	1.5	5.6	—
³ E _{1u} (³ Γ ₁₂)	2.2	5.8	0.8	4.3	—
³ B _{1u} (³ Γ ₉)	1.5	4.5	0.2	3.0	3.8*
¹ A _{1g} (¹ Γ ₁)	0.0	0.0	0.0	0.0	0.0

^a I denotes incorrect integrals (see reference 5); N denotes neglect of hybrid, exchange, and penetration integrals involving non-neighboring carbon atoms.

¹ Reference 1.

² Reference 3.

³ References 6 and 7.

⁴ These values have been calculated independently by both authors, and have been essentially confirmed by Mulliken [R. S. Mulliken, "Report on Molecular Orbital Theory," J. de Chim. Phys. (to be published)].

⁵ Reference 2.

⁶ The investigations of H. Shull, J. Chem. Phys. 17, 295 (1949) and D. S. McClure, J. Chem. Phys. 17, 665 (1949), indicate that this observed level may have the symmetry ³B_{2u}. If this is the case, the calculated triplet levels fall in the wrong order, since the 3.8 ev level is definitely the lowest triplet level (see reference 2).

peated,^{6,7} the energies which are found are bad (see fourth column in Table I), but the energies one gets upon redoing the London calculation are very encouraging (see next to last column in Table I).

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Dynamic Properties of Polymeric Materials

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August 17, 1949

CONSIDERABLE interest is attached to the problem of the mechanical properties (dynamic modulus G_{dyn} and dynamic viscosity η_{dyn}) of high polymers subjected to harmonic vibrations of varying frequencies. In particular, it has been observed that $\eta_{dyn}\omega$ is relatively independent of frequency $\omega/2\pi$ over a considerable frequency range.¹⁻⁴ The question has also arisen as to whether a relationship exists between the dynamic energy losses and static phenomena such as creep.

Kuhn has shown how, in a material for which the creep curve is linear with logarithmic time, one may predict the dynamic losses in free vibration experiments.⁵ In the course of his theoretical arguments he described the mechanical system approximately in terms of a distribution of relaxation times which is a rectangular function on a logarithmic plot, namely,

$$G(\tau)d(\log\tau) = \begin{cases} G_0 & a < \tau < b \\ = 0 & a > \tau, \tau > b \end{cases} \quad (1)$$

This distribution of relaxation times had previously been extensively investigated by Becker for ferromagnetic hysteretic behavior.⁶ The same function was also shown to fit stress relaxation data in polyisobutylene.⁷

By use of the distribution function (1), the correlation between stress relaxation and dynamic properties is exact and remarkably simple, and is mathematically even more direct than the correlation between creep data and dynamic properties. If stress relaxation is linear when plotted against logarithmic time, the data can be expressed in terms of the distribution function (1), where a and b are, respectively, smaller than and greater than the smallest and largest recorded times. For dynamic experiments in which $1/b \ll \omega \ll 1/a$, the following very simple relationship exists:

$$\eta_{dyn}\omega = \frac{\pi}{2\epsilon_0 \log_e 10} \quad (\text{slope of relaxation curve plotted vs. } \log_{10} \text{ time}), \quad (2)$$

where ϵ_0 is the fixed strain at which the stress relaxation measurement is being carried out.

This relationship was applied to stress relaxation data⁸ for rubbers, and the predicted values of $\eta_{dyn}\omega$ were compared with observed values of $\eta_{dyn}\omega$ for the same rubber stocks.³ Also experimental data were obtained for stress relaxation and dynamic properties of various textile fibers, and comparison between $\eta_{dyn}\omega$ values predicted from Eq. (2) and observed values was made. These comparisons are shown in Table I. It is clear from this table that an order of magnitude agreement exists between the observed and calculated values. In most cases the losses predicted from stress relaxation data are less than the observed dynamic losses. Papers detailing the theoretical and experimental developments will appear soon in the *Textile Research Journal*.

TABLE I.

Material	Temp. °C	Calc'd η_{dyn}^{ω} dynes/cm ²	Observed η_{dyn}^{ω} dynes/cm ²
Hevea gum stock	40°	0.026 × 10 ⁶	0.24 × 10 ⁶
	100°	0.045 × 10 ⁶	0.13 × 10 ⁶
Hevea tread stock	40°	0.48 × 10 ⁶	2.5 × 10 ⁶
	100°	0.55 × 10 ⁶	1.1 × 10 ⁶
GR-S gum stock	40°	0.11 × 10 ⁶	0.85 × 10 ⁶
	100°	0.11 × 10 ⁶	0.42 × 10 ⁶
GR-S tread stock	40°	1.1 × 10 ⁶	7.8 × 10 ⁶
	100°	0.40 × 10 ⁶	3.0 × 10 ⁶
Butaprene gum	40°	0.17 × 10 ⁶	1.7 × 10 ⁶
	100°	0.25 × 10 ⁶	0.70 × 10 ⁶
Butaprene tread	40°	0.42 × 10 ⁶	4.1 × 10 ⁶
	100°	0.40 × 10 ⁶	1.5 × 10 ⁶
Neoprene gum	40°	0.33 × 10 ⁶	0.85 × 10 ⁶
	100°	0.33 × 10 ⁶	0.68 × 10 ⁶
Neoprene tread	40°	0.82 × 10 ⁶	3.9 × 10 ⁶
	100°	0.86 × 10 ⁶	2.0 × 10 ⁶
Nylon	20°	0.8 × 10 ⁹	3.8 × 10 ⁹
Viscose rayon	20°	1.4 × 10 ⁹	4.8 × 10 ⁹
Acetate rayon	20°	1.2 × 10 ⁹	1.5 × 10 ⁹
Feather keratin	20°	0.70 × 10 ⁹	1.5 × 10 ⁹
Raw silk	20°	2.3 × 10 ⁹	3.8 × 10 ⁹
Polyethylene	20°	0.18 × 10 ⁹	0.82 × 10 ⁹

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A Kinetic Mechanism for Ion-Exchange

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It has generally been observed that the velocity of the zeolitic exchange of monovalent ions in dilute solution obeys simple mass action rate equations.¹⁻⁴ It does not necessarily follow, however, that a chemical exchange process is rate controlling. Thus, Boyd, Adamson, and Myers⁴ showed that for tracer exchange the observed mass action rate equation was predicted on the basis of diffusion through a bounding liquid film. This mechanism, moreover, explained the dependence of the exchange velocity on the particle size and stirring rate.

The present paper extends the film diffusion hypothesis to the more common case of exchange of macro-concentrations of both ions. The equilibrium constant for the exchange process $A^+ + BR = AR + B^+$ may be written as

$$K = \bar{C}_B N_A / \bar{C}_A N_B. \quad (1)$$

The thermodynamic activities have been assumed equal to the molar concentrations in solution and to the mole fractions N_A and N_B in the resin phase.

The permeation of the ions through the liquid film is given by Fick's first law

$$\begin{aligned} P_A &= -D_A(\partial C_A / \partial l) = D_A(C_A - \bar{C}_A) / l \\ P_B &= -D_B(\partial C_B / \partial l) = D_B(C_B - \bar{C}_B) / l. \end{aligned} \quad (2)$$

It is assumed that the concentrations of A^+ and B^+ vary linearly from C_A and C_B , the average solution concentrations, to \bar{C}_A and \bar{C}_B at the surface of the resin particle, over a region of effective thickness l . \bar{C}_A and \bar{C}_B are taken to be those concentrations in equilibrium with the instantaneous composition of the exchanger,

and hence by (1)

$$\bar{C}_A = \bar{a} / (1 + \bar{C}_B / \bar{C}_A) = \bar{a} / (1 + K N_B / N_A), \quad (3)$$

where $\bar{a} = \bar{C}_A + \bar{C}_B$. It follows, by a material balance, that

$$\Sigma P_A = d(\chi \bar{C}_A) / dt + d(E N_A) / dt \quad (4)$$

$$\Sigma(P_A + P_B) = d(\chi \bar{a}) / dt, \quad (5)$$

where Σ is the surface area/g of resin of exchange capacity E equivalents/g, and χ is the "interstitial" volume/g. The variations in $\chi \bar{C}_A$ and $\chi \bar{a}$ can be neglected if the solution is dilute, so to a first approximation, the net transfer rate may be set equal to zero, i.e. $P_A + P_B = 0$. By means of (2), (3), and (5) it follows that

$$\bar{a} = \frac{(D_A C_A + D_B C_B)(K N_B + N_A)}{D_A N_A + K D_B N_B} \quad (6)$$

and then from (2), (3), (5), and (6), the permeations of the two ions are

$$P_A = -P_B = \frac{D_A D_B (K C_A N_B - C_B N_A)}{l(D_A N_A + K D_B N_B)}. \quad (7)$$

Setting $d(\chi \bar{C}_A) / dt = 0$ in Eq. (4), the differential rate equation becomes

$$dN_A / dt = \frac{\Sigma D_A D_B (K C_A N_B - C_B N_A)}{El(D_A N_A + K D_B N_B)}. \quad (8)$$

Two cases will be considered. For constant outer solution concentration, (8) becomes

$$dN_A / dt = \frac{\Sigma D_A [C_A^0 - (C_A^0 + C_B^0 / K) N_A]}{El[1 + (D_A / K D_B - 1) N_A]} \quad (9)$$

and for variable solution concentration, where $C_B = 0$ and $C_A = C_A^0$ at $t = 0$

$$dN_A / dt = \frac{\Sigma W D_A [K(1 - N_A)(C_A^0 V / WE - N_A) - N_A^2]}{VKl[1 + (D_A / K D_B - 1) N_A]} \quad (10)$$

where V is the total volume of solution and W the weight of ion-exchanger. The quantity $D_A / K D_B$ is of the order of unity for the exchange of monovalent ions, and if N_A remains small throughout the exchange reaction, the bracketed expression in the denominator may be set equal to unity. With this approximation, (8) becomes a mass action type rate equation and the special cases, (9) and (10), give on integration

$$\ln(1 - N_A / N_A^\infty) = -kt \quad (11)$$

$$\frac{N_A^\infty}{2\alpha - (1 + \alpha)N_A^\infty} \frac{\ln \alpha(N_A + N_A^\infty) - (1 + \alpha)N_A^\infty N_A}{\alpha(N_A^\infty - N_A)} = k't, \quad (12)$$

where $\alpha = C_A^0 V / WE$. N_A^∞ is the mole fraction of A^+ on resin sites at equilibrium, and k and k' are

$$k = \frac{\Sigma D_A C_A^0 N_A^\infty}{El} \quad (11a)$$

$$k' = \Sigma W D_A / Vl. \quad (12a)$$

Equations (11) and (12) are identical with the first and second order mass action equations that have been observed experimentally, except for the different significance of the rate constants, (11a) and (12a).

This demonstration of the similarity of the film diffusion and mass action equations makes it apparent that the presently available rate data does not permit differentiation between film diffusion and chemical exchange as the rate controlling process. Such differentiation would be possible, however, under conditions such that the expression in the denominator of (9) cannot be taken as unity. Thus, the complete integral of (9) is

$$\begin{aligned} \ln\left(1 - \frac{N_A}{N_A^\infty}\right) + \frac{C_A^0(D_A - K D_B)N_A}{(C_A^0 D_A + C_B^0 D_B)N_A^\infty} \\ = -\frac{\Sigma D_A D_B (K C_A^0 + C_B^0) C_A^0}{El N_A^\infty (C_A^0 D_A + C_B^0 D_B)} t \end{aligned} \quad (13)$$