Condensation Coefficient and Adsorption

Hans M. Cassel

TABLE I.

No.	Molecular weight of fractions	Composition of the mixture by weight	10^{-3}				
			E.E.M.W.	M_{St}	M_n	M_w	M_z
8	75	9.62	30.0 ± 1	27.8	21.5	25.3	35.7
	20	90.38					
9	220	88.4	250 ± 35	207	8.3	194	220
	1	11.6					
10	220	46.0	170 ± 15	148	1.8	101	219
	1	54.0					
11	220	13.15	125 ± 10	102	1.15	29.9	189.5
	1	86.85					

tions, one can obtain the experimental equivalent molecular weight of the fraction-mixture (E.E.M.W.). The E.E.M.W. can be then compared to calculated $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ values and to the molecular weight of the hypothetical fraction $\bar{M}_{St}$, that according to (1) would have the same precipitation point as the mixture used.

$\bar{M}_{St}$ was calculated from:

$$(1 + x_{St}^{-1/2})^2 = 2\mu_c = (1 + x_w^{-1/2})^2 - \frac{(x_z^{1/2} - x_w^{1/2})^2}{x_w \cdot x_z^{1/2}}. \qquad (2)$$

Table I gives the results obtained in a few characteristic cases (all the molecular weights in thousands). The agreement between E.E.M.W. and M_{St} without being perfect is much better then between E.E.M.W. and the other averages and can be judged as satisfactory, in view of the unavoidable errors in the molecular weights of fractions.

[1] G. Gavoret and M. Magat, J. Chimie Phys. (to be published).
[2] R. L. Scott, J. Chem. Phys. **13**, 178 (1945). M. Magat, J. Chimie Phys. to be published.
[3] W. H. Stockmayer, J. Chem. Phys. **17**, 588 (1949).
[4] In the note published by Stockmayer the sign before the second term is given as positive but from the context one can deduce that in reality it should be negative.


A Preferentially Oil Soluble Carrier for Radiocobalt-60

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A FREQUENTLY met with industrial problem is the quantitative measurement of the location and flow of liquids through porous media or behind barriers to visibility and access. One attack on this measurement problem is to incorporate a gamma-active material in the liquid and to trace the movement of the liquid with a Geiger counter or other radiation detector located externally to the system barriers. When the flowing liquid consists in mutually little soluble liquid pairs, such as water and oil, it is generally desirable that the gamma-active tracer be confined to only one liquid phase.

The cobaltous salt of the dodecyl ester of tetrahydrophthallic acid, having the structural formula,
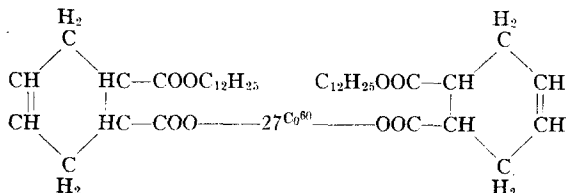
is suitable for carrying the gamma-activity of radiocobalt-60 into oils in a highly preferential manner. This salt possesses the following properties as a carrier:

1. Solubility to the extent of 1.5 percent by weight of the salt in acid washed kerosene at 25°C.

2. A kerosene over water distribution coefficient in excess of 200 at 25°C provided that the water have a pH of seven and not contain cations exchangeable with cobaltous ion.
3. Thermal stability to temperatures in excess of 100°C.
4. Hydrolytic stability in contact with water at pH-7.
5. Stability toward photolysis provoked by sunlight.

This organic salt has been synthesized from samples of Atomic Energy Commission irradiated cobaltic oxide (Co_2O_3). The oxide has been digested to solution with $12N$ hydrochloric acid and adjusted to pH-5 with sodium hydroxide solution. A water solution of the sodium salt of the organic acid has been admixed with the cobaltous chloride solution in appropriate mole proportions, whence the cobaltous salt of the organic acid precipitates. The precipitated salt suspended in the water phase has been directly extracted into a desired oil by gentle agitation of contacting phases of oil and water containing suspended salt. Any excess cobaltous chloride has then been removed from the oil phase by repeated water washing. Large samples of oil containing as much as 0.03 mc/ml have been prepared by this procedure.

Condensation Coefficient and Adsorption

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THE condensation coefficient, defined as the ratio, α, of the observed rate of evaporation to the gas kinetically computed excess of molecules striking the surface of the condensed phase per unit time, has recently been discussed by G. Wyllie[1] from the standpoint of Volmer's theory of phase transitions.[2] Accordingly, evaporation and condensation have to be considered as (at least) two-step processes, the exchanged molecules passing through the adsorbed state at the interface. To describe the rate of transition from the substrate into the adsorbed film Wyllie introduces the simplest possible hypothesis, namely that this is given by $A(\Gamma_0 - \Gamma)$, where A depends on the temperature, and Γ is the superficial concentration, the subscript referring to the state of equilibrium. Regarding the exchange between the film and the vapor phase he assumes that the adsorption isotherm is that of an ideal two-dimensional gas: $\Gamma = \tau b p$. Here, τ is the "verweilzeit"[3] in the adsorbed state, determining the rate of desorption, $b = (2\pi mkT)^{-\frac{1}{2}}$, and p is the vapor pressure. On this basis, Wyllie derives the expression

$$\alpha = A/(1/\tau + A).$$

It is quite obvious that the restriction to low pressure adsorption limits the validity of this theory unnecessarily, and that a better approximation can be obtained on the assumption of a Langmuir type adsorption isotherm

$$\Gamma = \tau b p / (1 + \tau \beta b p). \qquad (1)$$

This implies that the occupied fraction of the surface, $\beta\Gamma$, is blocked to impinging molecules, and the condensation efficiency correspondingly reduced. On this basis, the result is

$$\Gamma = (A\Gamma_0 + bp)/(1/\tau + A + \beta b p) \qquad (2)$$

and

$$\alpha = A/(1/\tau + A + \beta b p)(1 + \tau \beta b p_0). \qquad (3)$$

This means that α becomes dependent on the pressure and, therefore, must be smaller for condensation than for evaporation. It should be noticed that the factor $(1 + \tau \beta b p_0)$, being always greater than $(1 + \beta \Gamma_0)$, may surpass the amount 2 if τ is great enough. Provided that $1/\tau$ can be neglected in comparison to A, the maximum condensation coefficient that may be attained is

$$\alpha_{max} = 1/(1 + \tau \beta b p_0). \qquad (4)$$

One has to be aware that Langmuir type adsorption can be expected only at temperatures higher than the critical temperature of the film which in the case of van der Waals' forces is half the critical temperature of its substance in bulk.[4] At lower temperatures the cohesive interaction between adatoms will contribute to

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,[5, 6] 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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[3] Leonard B. Loeb, Kinetic Theory of Gases (McGraw-Hill Book Company, Inc., New York, 1927), p. 330.
[4] H. M. Cassel, J. Phys. Chem. 48, 195 (1944).
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[6] W. Prueger, Zeits. f. Physik 115, 202 (1940).

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 experiment[2] (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 repeated,[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).

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

Level	Goeppert-Mayer Sklar[b] (I, N)[a]	London[c] (I)[a]	Craig Parr[d] (N)[a]	Roothaan Parr[e]	Observed[f]
$^1E_{1u}(^1\Gamma_{12})$	8.0	11.1	6.7	9.7	7.0
$^1B_{1u}(^1\Gamma_{10})$	5.8	8.8	4.2	7.2	6.2
$^1B_{2u}(^1\Gamma_9)$	5.0	7.3	3.7	5.8	4.9
$^3B_{2u}(^3\Gamma_{10})$	3.0	7.2	1.5	5.6	—
$^3E_{1u}(^3\Gamma_{12})$	2.2	5.8	0.8	4.3	—
$^3B_{1u}(^3\Gamma_9)$	1.5	4.5	0.2	3.0	3.8g
$^1A_{1g}(^1\Gamma_1)$	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.
b Reference 1.
c Reference 3.
d References 6 and 7.
e 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)].
f Reference 2.
g 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).

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[7] D. P. Craig, "Polar Structures in the theory of conjugated molecules, Part 4" (to be published). We are greatly indebted to Dr. Craig for allowing us to see his manuscript.

Dynamic Properties of Polymeric Materials

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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,

$$G(\tau)d(\log\tau) = G_0 \quad a < \tau < b \atop = 0 \quad a > \tau, \tau > b \} . \tag{1}$$

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:

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

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

This relationship was applied to stress relaxation data[8] 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.