template, if they are to be assigned unambiguously. Moreover a well-known result from communication theory asserts that no unique code representation of an ensemble of events can reduce their information measure[4-6]. Information is measured in this context by use of the binary logarithm of probability, a particularly perspicuous form for mixing entropy. Thus, no uniquely determined polymer standard can exceed the orderliness of the template from which it was synthesized—a result that is in accord with the second law of thermodynamics.

A significant feature of equation (6) to be accounted for is the theoretical consequence of subtracting a component of the mixing entropy in a series of independent reactions from the reaction entropies. It is to be observed that the relationship extends the domain of entropy from that in classical thermodynamics and communication theory; indeed it links the entropy of energy with pure configuration entropy. Since in theory the mixing entropy of non-interacting reactants can be increased arbitrarily, no natural limit exists on the magnitude of the entropy. Apparently the second law of thermodynamics is inapplicable to the overall change in entropy during template-directed polymerization. However, as equilibrium is specified by the first term of equation (6) it may be deduced that the mixing entropy of the second term is not transmutable to free energy.

I thank Dr. Paul Doty for the opportunity to work in his laboratory.

B. K. Davis*

Department of Chemistry,
  Harvard University,
    Cambridge,
      Mass.

* Present address: Medical Research Council Laboratory of Molecular Biology, University Postgraduate Medical School, Cambridge, England.

[1] Wolkenshtein, M. V., and Eliasevich, A. M., *Biophys.*, **6**. 5, 1 (1961).
[2] Messelson, M., and Stahl, F. W., *Proc. U.S. Nat. Acad. Sci.*, **44**, 671 (1958).
[3] Richardson, C. C., Schildkraut, C. L.' and Kornberg, A., *Cold Spring Harbor Symp. Quant. Biol.*, **28**, 9 (1963).
[4] Shannon, C. E., *Bell Syst. Tech. J.*, **27**, 379, 623 (1948).
[5] Kinchin, A. I., *Mathematical Foundations of Information Theory* (Dover, New York (1957).
[6] Fano, R. M., *Transmission of Information* (M.I.T. Press, 1961).

Entropy of Activation of Viscous Flow in Dilute Solutions of High Polymers

It has been previously shown[1,2] that the entropy of activation of viscous flow, ΔS, of dilute solutions of flexible chain high polymers decreases with increasing concentration c and molecular weight M of the polymer. In contrast, ΔS for dilute solutions of cellulose derivatives, the chains of which are stiffer and more extended in solution[3], generally increases with increase of c and M (refs. 1, 2 and 4). An interpretation in terms of positive and negative contributions to ΔS was tentatively advanced[2]. The positive contribution was assumed to be proportional to Q/T, where Q is the apparent activation energy of viscous flow of the solution and T the absolute temperature. The negative contribution was assumed to be not primarily dependent on Q and to result from synchronization between movements necessary for a successful unit act of flow[5]. The effects of variation in c and M on Q are relatively small for dilute solutions of flexible chain high polymers and it was suggested that the negative contribution was the greater. The marked increases in Q with increase of C or M, observed with dilute solutions of cellulose derivatives, led to the suggestion that in such cases increases in the positive contribution outweighed any increases in the negative one.

The use of rate process theory as applied to the flow of high polymer molecules[6,7] may provide a clearer picture of the nature of these contributions to ΔS and a more precise interpretation of the variations of ΔS with c and M. It is generally accepted that the flow of flexible high polymer chains in polymer melts involves successive movements of chain segments each of which is 30–50 carbon atoms in length[6]. Kauzmann and Eyring[6] have given an expression for ΔS for a single chain that may be written in a general form:

$$\Delta S = x - yf(M) \qquad (1)$$

where x and y are constants for a given flexible chain polymer and $f(M)$ a function of its molecular weight. x, which depends on the size of a segment, represents the gain in entropy on activation of a segment and $-yf(M)$ a loss in entropy arising from the necessity for co-operation between chain segments in order that the chain may move as a whole. Assuming that the movement of a single chain in the flow of a dilute solution is similar to that of a chain in the melt, equation (1) will represent the contribution made by the chain to ΔS for the solution. With flexible chain polymers containing many segments per chain, x is likely to be small and will generally be exceeded by $yf(M)$ as in the case of polymer melts[6,7]. ΔS for the solution will therefore decrease with increase of c, increasing the number of chains, and M, increasing the number of chain segments.

With stiff and extended cellulose derivatives the size of the segment acting as a unit in flow, and therefore x, is likely to be much larger. The activation energy of viscous flow is also dependent on segment size[6,7] and the contributions made by cellulose derivatives to Q are ten to a hundred times greater than those made by flexible chain polymers[2]; $yf(M)$ should be much smaller and ΔS for the solution should therefore be positive. It is possible that with cellulose derivatives the unit in flow may be the whole chain rather than a segment of it and this would explain the fact that, for a given concentration of polymer, ΔS increases with both M and the degree of extension of the cellulose derivative chains. In such circumstances the negative contribution to ΔS may be zero or negligible.

W. R. Moore

Polymer Research Laboratories,
Department of Chemical Technology,
Bradford Institute of Technology.

[1] Moore, W. R., *Nature*, **191**, 1292 (1961).
[2] Fort, R. J., Hutchinson, R. J., Moore, W. R., and Murphy, M., *Polymer*, **4**. 35 (1963).
[3] Immergut, E. H., and Eirich, F. R., *Industr. Eng. Chem.*, **45**, 2500 (1953).
[4] Moore, W. R., and Brown, A. M., *J. Colloid Sci.*, **14**, 1 (1959).
[5] Barrer, R. M., *Trans. Faraday Soc.*, **39**, 48 (1943).
[6] Kauzmann, W., and Eyring, H., *J. Amer. Chem. Soc.*, **62**, 3113 (1940).
[7] Powell, R. E., and Eyring, H., *Advances in Colloid Science*, **1**, 199, edit. by Kraemer, E. O. (Interscience, New York, 1942).

Theoretical Study of Benzologues of 4-Thiapyrone

Polycyclic compounds containing the 4-pyrone nucleus occur in plants as the tannins and have been extensively studied, but their sulphur analogues have received much less attention. We are studying the chemistry of benzologues of 4-thiopyrone and report here some theoretical studies of six of them (I-VI) made by the simple MO-LCAO method using the Hückel approximation, together with some correlations of the results with experimental data. The secular determinants were solved with the aid of an IBM 7074 digital computer using a standard programme, which was first tested with pyrene and pyridine for which results are already available in the literature[2].

For each of the four compounds, two models, A and B, were considered. In model A, participation of the d-orbital of the sulphur was assumed[3], and in the B model it was ignored. In the approximation used, the coulomb integral of the hetero-atoms and of carbon directly bonded to a hetero-atom is given by the relation $\alpha_x = \alpha_c + \delta_x\beta_{cc}$, and the resonance integral of the bonds between carbon and hetero-atom by $\beta_{cx} = \rho_{cx}\beta_{cc}$; the α's are coulomb integrals and the β's resonance integrals, and δ_x and ρ_{cx} are