On the Detection and Determination of Redundant Vibrational Coordinates

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is most likely brought about by the intertwining of at least two or more chain segments belonging to the same or to different chain molecules and it is obvious that temperature and external forces have a pronounced effect on the average lifetime of these net points which are much less stable than the net points due to chemical crosslinking. Without the assumption of a semipermanent network, it does not seem possible to account for the fact (a) that the birefringence stress ratio remains constant and the deformation is almost completely recoverable at the same time, (b) that the birefringence and the stress can relax by a factor 2 to 3 without destroying the ability of the material to recover to its original length, (c) that "cycling" has an effect on the stress and birefringence relaxation and the initial creep compliance, and (d) that polystyrene exhibits anomalous flow characteristics[2] at temperatures much above its softening temperature. More experimental data and a more thorough discussion of some of the results given above, such as the initial change of the birefringence-stress ratio with time, the relationship of birefringence to orientation, etc., will be published in the near future.

* All films were prepared following a technique previously described; see Abstracts in Proceedings of the American Physical Society Meeting at New York, Phys. Rev. **75**, 1279 (1949).

[1] T. Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948), pp. 93–228.

** Recently one of the authors suggested such a network structure on the basis of flow measurements on polystyrene at high temperature. (See J. Colloid Sci.)

[2] R. Buchdahl, J. Colloid Sci. **3**, 87 (1948).

On the Detection and Determination of Redundant Vibrational Coordinates*

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IN using valence-force coordinates (*VFC*) in a normal-coordinate treatment, one not infrequently finds it convenient, for symmetry reasons, to consider a redundant set; i.e., a set of coordinates which are not all independent. The neatest example is the set of six HCH angle deformations, $\Delta\alpha_{ij}$, in CH_4; these are of course connected by the *redundancy condition*

$$\sum_{i>j} \Delta\alpha_{ij}=0. \tag{1}$$

Wilson[1] has discussed such redundant coordinates, the possible ways of treating them, and the consequent restrictions on the potential energy.

While one usually knows or easily finds out that a set of coordinates is redundant, it is not always so easy to find the redundancy condition analogous to (1).[2] The purpose of this note is to present a convenient way to do this, using Wilson's *G* matrix technique.[1] In our practice we need to find this redundancy, for we prefer to transform from our initial *VFC* to a set of symmetry coordinates *one of which is precisely the redundancy;* both the *F* and *G* matrices are so transformed. Then the *G* matrix has a row and column of zeros,[1] which may be neglected together with the corresponding row and column of the *F* matrix.

If the redundancy condition is initially not known, we may still set up symmetry coordinates, found from the *VFC* by elementary group theory.[3] Moreover, the symmetry species containing the redundancy is easily found, either by noting which species has an extra coordinate, or (in case a needed coordinate has been inadvertently neglected and a redundant one unwittingly included) by observing that the *G* matrix factor for this species has a zero determinant.

Let S_k be the symmetry coordinates in which a redundancy lurks, so that $|G|=0$, where G is the inverse kinetic-energy matrix for the S_k. We seek to transform to the coordinates $\bar{S}_n$

such that $\bar{S}_1$ is the redundancy condition: $\bar{S}_1=0$. Let the transformation be orthogonal, so that

$$\bar{S}_n=\sum_k L_{nk}S_k, \tag{2}$$

$$\sum_n L_{nk}L_{nj}=\delta_{kj}. \tag{3}$$

Now if $\bar{G}$ is the inverse kinetic-energy matrix for the $\bar{S}_n$, $\bar{G}$ and G are related:

$$\bar{G}_{nm}=\sum_{jk} L_{nk}G_{kj}L_{mj}. \tag{4}$$

Moreover, since $\bar{S}_1$ is the redundancy,

$$\bar{G}_{1n}=\bar{G}_{n1}=0, \quad \text{all } n. \tag{5}$$

Hence, taking $m=1$ in (4), multiplying through by L_{ni}, summing on n and using (3), we find

$$\sum_j G_{ij}L_{1j}=0. \tag{6}$$

This tells us, then, how to find our redundancy condition $\bar{S}_1=\sum_j L_{1j}S_j=0$; if we regard our original G as the matrix of coefficients of a set of homogeneous linear equations, the transformation coefficients L_{1j} are just the "unknowns" whose ratios are determined. (Normalization completes the determination of the L_{1j}.) The remaining coefficients $L_{nk}(n\neq 1)$ may be written down as usual to make L orthogonal,[4] and the resulting L used to transform both F and G.

If a species contains, say, s redundancies among n coordinates $(s>1)$, then the G matrix factor will be of order n but of rank $(n-s)$. The usual algebraic procedures[5] for treating linear homogeneous equations will then give us the s sets of redundancy coefficients $L_{1j}, L_{2j}, \cdots, L_{sj}$.

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[1] E. Bright Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

[2] The reader complacent about geometry may write down the redundancy conditions among the six C-C distances and six C-C-C angles in cyclohexane.

[3] E. P. Wigner, *Gruppentheorie* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1944); p. 123.

[4] *Inter alia,* reference 3, p. 31.

[5] Bocher, *Higher Algebra* (The Macmillan Company, New York, 1907); Chapter IV.

The Methylene Radical

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IN a recent Letter to the Editor Laidler and Casey[1] discuss the methylene radical, CH_2. They state that since the bond angle in the lowest state is about 140°, this state cannot be a triplet state. However, one may use hybrid orbitals for the two unshared electrons as well as for the two shared electron pairs.

Thus one may use the sp^3 hybrid orbitals[2] appropriate to AB_2C_2 for the covalent triplet structure. If Pauling's criterion[3] of strength is employed and if the interaction energy[4] of a shared electron pair equals that of an unshared electron, one would expect the tetrahedral structure (the structure with the H-C-H angle equal to 109° 28') to be the most stable of the triplet structures.

The covalent singlet structure may be discussed as follows. Set up the functions appropriate to AB_2C, where A is the central atom, assuming the bonds lie in a plane. Thus

$$\psi_1=a_1s+b_1p_x, \tag{1}$$

$$\psi_2=a_2s-b_2p_x+c_2p_y, \tag{2}$$

$$\psi_3=a_3s-b_3p_x-c_3p_y. \tag{3}$$

Here ψ_1 describes the orbital occupied by the unshared electron pair, and ψ_2 and ψ_3 describe the orbitals used in forming the bonds.

The orthogonality and normalization conditions together with the equation $a_2 = a_3$ yield

$$c_2 = c_3 = \frac{1}{\sqrt{2}}, \tag{4}$$

$$b_2 = b_3 = (\tfrac{1}{2} - a_2^2)^{\frac{1}{2}}. \tag{5}$$

The constants a_1 and b_1 can be expressed in terms of a_2 also. The functions ψ_2 and ψ_3 depend on the parameter a_2. They are strongest when the angle between their maxima, θ, equals the tetrahedral angle and their strength, S, equals that of tetrahedral bonds. This singlet structure does not require the promotion of an s electron since it requires no contribution from p_z. Hence it should be more stable than the triplet structure. The conclusion is supported by the experimental work cited by Laidler and Casey.[1]

If we assume θ equals 140° in the singlet structure, we find that a_2 equals 0.659 and S equals 1.962. Now S equals 2.000 when θ equals 109° 28'. The 140° structure might be stabilized by the ionic character of the bonds. An alternative explanation is that Pauling's criterion of strength underestimates somewhat the contribution from the s orbital to the stability of the bonds.[5]

[1] K. J. Laidler and E. J. Casey, J. Chem. Phys. **17**, 213 (1949).
[2] G. H. Duffey, J. Chem. Phys. **14**, 342 (1946).
[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).
[4] See H. Kuhn, J. Chem. Phys. **16**, 727 (1948).
[5] See R. S. Mulliken *et al.*, J. Chem. Phys. **17**, 510 (1949). The author has received a private communication (1949) from A. Maccoll of University College, London regarding the same subject.

# Near-Equilibrium Criteria for Complex Chemical Reactions during Flow through a Nozzle*

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CALCULATIONS of the effect of vibrational and chemical lags on the exhaust velocity of the combustion products formed in conventional rocket motors have been restricted previously[1] to a consideration of individual processes without the introduction of corrections for the interdependence of the chemical reactions or of the vibrational distributions. The approach to chemical equilibrium for a number of interdependent chemical reactions can be handled, at least in principle, by a straightforward generalization of the techniques described previously. Calculations on complex systems require the solution of a number of simultaneous linear and non-linear equations.

Non-linear relations between the temperature lags in complex systems. Consider a system of chemical reactions of $n-1$ individual steps leading to the over-all reaction shown in the n'th step, as follows:

$$\alpha_j + \beta_j + \cdots \rightleftarrows \gamma_j + \delta_j + \cdots, \quad j = 1, 2, \cdots, n.$$
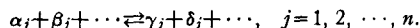
The statement that step n is the sum of steps 1 to $n-1$ means that

$$\alpha_n + \beta_n + \cdots = \sum_{i=1}^{n-1} \alpha_i + \sum_{i=1}^{n-1} \beta_i + \cdots;$$

$$\gamma_n + \delta_n + \cdots = \sum_{i=1}^{n-1} \gamma_i + \sum_{i=1}^{n-1} \delta_i + \cdots.$$

Furthermore, if K_j^0 ($j = 1, 2, \cdots, n$) denotes the equilibrium constant for the j'th step, then

$$K_n^0 = \prod_{i=1}^{n-1} K_i^0.$$

During the adiabatic expansion through a nozzle thermodynamic equilibrium is not maintained with respect to the n chemical reactions described above. Each of the n reactions, considered individually, suffers a temperature lag which is designated as $T_j - T$ and defined by the relation

$$K_j = \frac{\Pi\text{-molecular concentrations of the species formed in step } j}{\Pi\text{-molecular concentrations of the species reacting in step } j}$$

where K_j is the equilibrium constant for the j'th step not at the true temperature T, but at a temperature T_j which differs from T. If the temperature lag $T_j - T$ is sufficiently small, then it is said that step j is in near-equilibrium. From the definition of K_j it is evident that

$$K_n = \prod_{i=1}^{n-1} K_i. \tag{2}$$

The quantities K_j may be expressed[1] in terms of the quantities K_j^0 by making use of a Taylor series; if $T_j - T$ is sufficiently small, all but the first two terms of the Taylor series may be neglected. Therefore

$$K_j = K_j^0 + K_j^0 \frac{d \ln K_j^0}{dT}(T_j - T). \tag{3}$$

Replacing K_j in Eq. (2) by its value from Eq. (3) it can readily be shown that

$$T_n - T = \sum_{i=1}^{n-1} \frac{d \ln K_i^0/dT}{d \ln K_n^0/dT}(T_i - T) + \sum_{i < m=2}^{m=n-1} \frac{d \ln K_i^0/dT}{d \ln K_n^0/dT}$$
$$(d \ln K_m^0/dT)(T_i - T)(T_m - T) + \cdots$$
$$+ \prod_{i=1}^{n-1} \frac{d \ln K_i^0/dT}{d \ln K_n^0/dT}(T_i - T). \tag{4}$$

Equation (4) is the desired result, since it gives an analytic expression for the temperature lag $T_n - T$ in terms of the temperature lags of the individual $n-1$ steps provided near-equilibrium is maintained with respect to each of the n individual reactions.

Linear relations between the temperature lags in complex systems. The linear relations between the temperature lags in complex systems involve the individual rate constants for each of the steps of a complex chemical reaction. It is possible to write one equation which is linear in the terms $T_j - T$ for each of the steps of a complex reaction. The number of independent linear equations is equal to the number of chemical reactions which cannot be constructed by simple additions or subtractions involving other chemical reactions which are known to be independent in this sense.

The linear equations can be obtained by following the procedure outlined previously[1] taking care, however, to allow for the simultaneous participation of a given reactant in several alternative reaction paths. A representative result obtained from Eq. (5) for the set of reactions

$$2H + M \rightleftarrows H_2 + M \tag{5}$$
$$H_2 + F \rightleftarrows HF + H \tag{6}$$
$$2F + M \rightleftarrows F_2 + M \tag{7}$$
$$H + F_2 \rightleftarrows HF + F \tag{8}$$
$$H + F + M \rightleftarrows HF + M \tag{9}$$
$$H_2 + F_2 \rightleftarrows 2HF \tag{10}$$

is

$$[\Delta H_5 - \gamma RT(\gamma - 1)^{-1}](-dT/dt)$$
$$= k f_5(M)(\Delta H_5 - RT)[1/K_5 + 2(H)](T_5 - T)$$
$$- k f_6(F)[1 + 2(H_2)/(H)](T_6 - T)$$
$$+ 2 k f_8(F_2)(\Delta H_8)(T_8 - T) + 2 k f_9(F)(M)$$
$$\times [\Delta H_9 - RT](T_9 - T) - k f_{10}(F_2)(\Delta H_{10})(T_{10} - T) \tag{11}$$

where the contributions to the concentration changes resulting from the change of state during adiabatic expansion have been taken into account. Equations similar to Eq. (11) can be derived readily from Eqs. (6) to (10). However, of the six linear equations involving the temperature lags $T_5 - T$ to $T_{10} - T$ only three are independent. This must be true, since it is possible, for example, to derive Eqs. (6), (8), and (10) from Eqs. (5), (7), and (9). A sufficient number of relations between the temperature lags