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On Thermodynamic Coupling of Chemical Reactions

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Any set of net chemical reactions in which thermodynamic coupling occurs can always be transformed by linear combination into a thermodynamically equivalent set in which such coupling does not occur, and conversely. Therefore the physical interest of thermodynamic coupling considered without reference to reaction mechanism is doubtful.

Introduction

We consider a closed system of σ constituents, $Q_1\cdots Q_\sigma$, whose mole numbers, $n_1\cdots n_\sigma$, are changing spontaneously at rates accountable for in terms of ρ linearly independent net chemical reactions, whereby $2 \le \rho < \sigma$, and the chemical equations of the reactions are, in De Donder notation

$$\sum_{i=1}^{\sigma} \nu_{ij}Q_i = 0, j = 1\ldots\rho \tag{1}$$

This means that the reactions themselves have rates, $v_1\ldots v_\rho$, which are given as the solutions of the equations[2]

$$\sum_{j=1}^{\rho} \nu_{ij}v_j = \frac{dn_i}{dt}, i = 1\ldots\sigma \tag{2}$$

The existence of these solutions in all cases is guaranteed by the linear independence of the reactions, i.e., of the ρ sets of σ coefficients each

$$\begin{matrix} \nu_{11}\ldots\nu_{\sigma 1} \\ \cdot \qquad \cdot \\ \cdot \qquad \cdot \\ \cdot \qquad \cdot \\ \nu_{1\rho}\ldots\nu_{\sigma\rho} \end{matrix} \tag{3}$$

We suppose furthermore that the temperature T and the chemical potential μ_i of each constituent are at each instant constant throughout the system. The reactions represented by eq. 1 are then known from thermodynamics to have affinities, $A_1\ldots A_\rho$, defined by

$$A_j = -\sum_{i=1}^{\sigma} \nu_{ij}\mu_i, j = 1\ldots\rho \tag{4}$$

We suppose finally that within the system no irreversible processes are occurring other than the aforementioned changes of the mole numbers, dn_i/dt.[3] The system is then known from thermodynamics to have a rate of entropy production, d_iS/dt, given by

$$\frac{d_iS}{dt} = \frac{1}{T}\sum_{j=1}^{\rho} A_jv_j \tag{5}$$

The product $T\dfrac{d_iS}{dt}$ is called the *power of irreversibility*

of the system; we shall denote it by P. Since T and d_iS/dt are each always positive or zero and the latter case does not concern us here, we have

$$P = \sum_{j=1}^{\rho} A_jv_j > 0 \tag{6}$$

This thermodynamic result admits of the possibility that one or more of the products A_jv_j be negative (at least one must of course be positive). In this case it is said that *thermodynamic coupling* occurs in the set of reactions represented by eq. 1 and that each member of the set is a *coupled* or a *coupling* reaction, according as its product A_jv_j is negative or positive. It is appealing to think of the coupling members of the set as *driving* each coupled member in the direction opposite to that suggested by its affinity. These ideas are all well known, frequently having been set forth by their originators, De Donder and the members of his school.[4] These authors have moreover claimed for thermodynamic coupling a high degree of physical interest on a number of grounds, not the least of which is that such coupling is "an essential feature of living systems."[5]

It is our purpose to call attention to a fundamental feature of thermodynamic coupling hitherto apparently overlooked. This feature arises from the fact, in itself entirely familiar, that the nature of the system determines the *number*, ρ, of the net chemical reactions needed to account for the changes $\dfrac{dn_i}{dt}$ in accord with eq. 2 but leaves the coefficients 3 indeterminate to the extent of an arbitrary linear combination. In other words, any set of chemical equations of type 1 derivable by linear combination of the members of a particular set satisfying eq. 2, likewise satisfies eq. 2. From this infinity of equivalent sets of reactions moreover, thermodynamics offers no criterion for a particular choice; this too is well known. What seems to have been overlooked is that as we pass from set to set, although the sum $\sum_{j=1}^{\rho} A_jv_j$ remains invariant, the number of the products A_jv_j having a given sign, and so the proportion of coupled to

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(2) We shall take the ν_{ij} to have the dimensions of mass and to be measured in moles. The rates v_j then have the dimensions of reciprocal time.

(3) The system is to be thought of as subject to any further conditions compatible with those just explicitly laid down. For example, we could require: (i) that the system be homogeneous, or alternatively, heterogeneous with some particular number of phases and (ii) that volume and temperature of the system be particular functions of time

$$V = V(t), T = T(t) \tag{4a}$$

and so forth. Conditions of type 4a are sometimes called "constraints." All such further conditions are however irrelevant to our ensuing discussion.

(4) T. De Donder, "L'Affinité," Paris, Gauthier-Villars (1927); Bull. Acad. Roy. Belg. Cl. Sci., 23, 770 (1937); T. De Donder and P. Van Rysselberghe, "Thermodynamic Theory of Affinity," Stanford University Press, 1936; P. Van Rysselberghe, Bull. Acad. Roy. Belg. Cl. Sci., 22, 1330 (1936); 23, 416 (1937); J. Phys. Chem., 41, 787 (1937); I. Prigogine and R. Defay, "Thermodynamique Chimique," 2 vols., Liège, Éditions Deoser, 1944, 1946; sec. ed. (1950); I. Prigogine and R. Defay, "Chemical Thermodynamics," translated by D. H. Everett, Longmans Green, New York, N. Y., 1954; I. Prigogine, "Thermodynamics of Irreversible Processes," C. C. Thomas, Springfield, Ill., 1955.

(5) I. Prigogine and R. Defay, ref. 4, p. 42.

coupling reactions, in general vary.[6] We shall show that it is always possible by linear combination to transform any set of reactions *with* thermodynamic coupling (one or more $A_j v_j < 0$) into a set *without* (all $A_j v_j > 0$), and conversely.[7] Thus the presence or absence of thermodynamic coupling in a given system undergoing chemical change will be seen to depend not upon the physico-chemical nature of the change but upon the choice of the chemical reactions taken to describe it. This conclusion plainly compels us to revise downward the aforementioned estimate of the physical interest of thermodynamic coupling.

Two Reactions.—We shall treat first the case $\rho = 2$. We consider a pair of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{i1} Q_i = 0 \tag{7.1}$$

$$\sum_{i=1}^{\sigma} \nu_{i2} Q_i = 0 \tag{7.2}$$

We suppose that thermodynamic coupling occurs in this pair, and take reactions 1 and 2 to be the coupled and coupling members, respectively; this means

$$A_1 v_1 < 0 \tag{8.1}$$
$$A_2 v_2 > 0 \tag{8.2}$$
$$P = A_1 v_1 + A_2 v_2 > 0 \tag{8.3}$$

We shall show that it is always possible to find a real number, α, such that the equivalent pair of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{i1} Q_i = 0 \tag{9.1}$$

$$\sum_{i=1}^{\sigma} (\nu_{i1} + \alpha \nu_{i2}) Q_i = 0 \tag{9.2}$$

is free of coupling; this means

$$A_1' v_1' > 0 \tag{10.1}$$
$$A_2' v_2' > 0 \tag{10.2}$$
$$P = A_1' v_1' + A_2' v_2' > 0 \tag{10.3}$$

where the primes refer to the new pair of reactions.

Proof: Equation 2 requires

$$\nu_{i1} v_1 + \nu_{i2} v_2 = \nu_{i1} v_1' + (\nu_{i2} + \alpha \nu_{i1}) v_2', \quad i = 1 \ldots \sigma \tag{11}$$

whence by solving simultaneously the two equations corresponding, respectively, to any two values of i, we find that the rates transform according to

$$v_1' = v_1 - \alpha v_2 \tag{12.1}$$
$$v_2' = v_2 \tag{12.2}$$

From eq. 4, 7.1, 7.2, 9.1 and 9.2 we find that the affinities transform according to

$$A_1' = A_1 \tag{13.1}$$
$$A_2' = A_2 + \alpha A_1 \tag{13.2}$$

It is readily verified that these equations of transformation leave P invariant, as required by eq. 8.3 and 10.3. We now suppose, as we evidently may without loss of generality, that eq. 7.1 and 7.2 are written in the directions which make

(6) If we consider the sets having a given reaction, say the k'th, in common, we see from eq. 4 that the affinity A_k is invariant and from eq. 2 that the rate v_k must in general vary from set to set. This variation can, as we shall see, change the sign of v_k and so of $A_k v_k$.

(7) T. De Donder, ref, 4 (1937), and I. Prigogine and R. Defay, ref. 4, (1944), p. 77, have considered transformations of the kind involved in our discussion but stopped short of our result.

$$v_1 > 0 \tag{14.1}$$
$$v_2 > 0 \tag{14.2}$$

This choice, in conjunction with ineq. 8.1 and 8.2, implies

$$A_1 < 0 \tag{15.1}$$
$$A_2 > 0 \tag{15.2}$$

Equation 13.1 and ineq. 15.1 imply

$$A_1' < 0 \tag{16}$$

Hence for the desired ineq. 10.1 to hold, it is necessary and sufficient that

$$v_1' < 0 \tag{17}$$

But this condition, by virtue of eq. 12.1 and ineqs. 14.1 and 14.2, is seen to be equivalent to

$$\alpha > \frac{v_1}{v_2} \tag{18}$$

Equation 12.2 and ineq. 14.2 imply

$$v_2' > 0 \tag{19}$$

Hence for the desired ineq. 10.2 to hold, it is necessary and sufficient that

$$A_2' > 0 \tag{20}$$

But this condition, by virtue of eq. 13.2 and ineq. 15.1 and 15.2, is seen to be equivalent to

$$\frac{A_2}{|A_1|} > \alpha \tag{21}$$

Ineq. 8.3 14.1, 14.2, 15.1 and 15.2 imply

$$\frac{A_2}{|A_1|} > \frac{v_2}{v_1} \tag{22}$$

Hence ineqs. 18 and 21 can hold simultaneously and constitute necessary and sufficient conditions for the desired ineq. 10.1 and 10.2. Thus α will produce the desired transformation if and only if it lies in the range

$$\frac{A_2}{|A_1|} > \alpha > \frac{v_1}{v_2} \tag{23}$$

and this condition can always be met. We note incidentally that since ineq. 14.1 and 14.2 imply $v_1/v_2 > 0$, ineq. 23 implies $\alpha > 0$.

For example, the synthesis of urea in liver, when written

$$2NH_3 + CO_2 = (NH_2)_2CO + H_2O$$
$$\frac{1}{6} C_6H_{12}O_6 + O_2 = CO_2 + H_2O$$
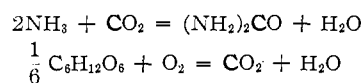
has been cited[8] as a case of thermodynamic coupling, with

$A_1 = -11$ kcal., $A_2 = 115$ kcal., $v_1 = 1.4 \times 10^{-8}$ min.$^{-1}$, $v_2 = 6.0 \times 10^{-8}$ min.$^{-1}$, $P = 6.7 \times 10^{-6}$ kcal. min.$^{-1}$

But this set can be transformed into one in which $A_1' v_1'$ and $A_2' v_2'$ are both positive: ineq. 23 yields $10.4 > \alpha > 0.24$; We may therefore choose $\alpha = 1$, which gives

$$2NH_3 + CO_2 = (NH_2)_2CO + H_2O$$
$$\frac{1}{6} C_6H_{12}O_6 + 2NH_3 = (NH_2)_2CO + 2H_2O$$
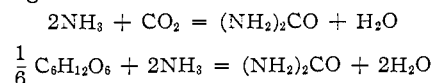
with

$A_1' = -11$ kcal., $A_2' = 104$ kcal., $v_1' = -4.6 \times 10^{-8}$ min.$^{-1}$, $v_2' = 6.0 \times 10^{-8}$ min.$^{-1}$, $P = 6.7 \times 10^{-6}$ min.$^{-1}$

(8) T. De Donder and P. Van Rysselberghe, ref. 4, (1937); I Prigogine and R. Defay, ref. 4, (1944), p. 74; see also H. Borsook and G. Keighley, *Proc. Natl. Acad. Sci. U. S.*, 19, 626, 720 (1933).

The converse of the proposition just proved and illustrated is also true. We consider a pair of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{i1}{}'Q_i = 0 \tag{24.1}$$

$$\sum_{i=1}^{\sigma} \nu_{i2}{}'Q_i = 0 \tag{24.2}$$

We suppose this pair to be free of thermodynamic coupling; this means

$$A_1{}'v_1{}' > 0 \tag{25.1}$$
$$A_2{}'v_2{}' > 0 \tag{25.2}$$
$$P = A_1{}'v_1{}' + A_2{}'v_2{}' > 0 \tag{25.3}$$

It is then always possible to find a real number, α', such that, of the equivalent pair of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{i1}{}'Q_i = 0 \tag{26.1}$$

$$\sum_{i=1}^{\sigma} (\nu_{i2}{}' + \alpha'\nu_{i1}{}')Q_i = 0 \tag{26.2}$$

the first member is coupled to the second; this means

$$A_1 v_1 < 0 \tag{27.1}$$
$$A_2 v_2 > 0 \tag{27.2}$$
$$P = A_1 v_1 + A_2 v_2 > 0 \tag{27.3}$$

where the unprimed letters refer to the new pair of reactions.

The proof of this proposition is so readily constructed by inverting step by step that given of the previous one, that we shall omit it, and state only the necessary and sufficient conditions on α' to which it leads. We suppose eq. 24.1 and 24.2 to be written in the directions which make

$$v_1{}' < 0 \tag{28.1}$$
$$v_2{}' > 0 \tag{28.2}$$

We then find that α' will produce the desired transformation if and only if

$$\alpha' < \frac{v_1{}'}{v_2{}'} \tag{29}$$

a condition which can obviously always be met, and which, since $\dfrac{v_1{}'}{v_2{}'} < 0$, implies $\alpha' < 0$.

The General Case.—The general case of ρ reactions, with $2 \le \rho < \sigma$, is resolvable by a treatment modeled upon that just accorded the case $\rho = 2$.

We consider ρ reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{ij}Q_i = 0, j = 1\ldots\rho \tag{30}$$

We suppose that, of this set, τ members, where $1 < \tau < \rho$, are coupled to the remaining $\rho{-}\tau$ members and that the set is so ordered that its first τ members are the coupled ones; this means

$$A_j v_j < 0, j = 1\ldots\tau \tag{31.1}$$
$$A_j v_j > 0, j = \tau + 1\ldots\rho \tag{31.2}$$

$$P = \sum_{j=1}^{\rho} A_j v_j > 0 \tag{31.3}$$

We shall show that it is always possible to find a

set of real numbers, $\alpha_1\cdots\alpha_{\rho-1}$, such that the equivalent set of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{ij}Q_i = 0, j = 1\ldots\rho - 1 \tag{32.1}$$

$$\sum_{i=1}^{\sigma} \left(\nu_{i\rho} + \sum_{j=1}^{\rho-1} \alpha_j\nu_{ij}\right)Q_i = 0 \tag{32.2}$$

is free of coupling[9]; this means

$$A_j{}'v_j{}' > 0, j = 1\ldots\rho \tag{33.1}$$

$$P = \sum_{j=1}^{\rho} A_j{}'v_j{}' > 0 \tag{33.2}$$

Proof: By considerations parallel to those leading to eq. 12.1 and 12.2, we find

$$v_j{}' = v_j - \alpha_j v_\rho, j = 1\ldots\rho - 1 \tag{34.1}$$
$$v_\rho{}' = v_\rho \tag{34.2}$$

and by considerations parallel to those leading to eq. 13.1 and 13.2, we find

$$A_j{}' = A_j, j = 1\ldots\rho - 1 \tag{35.1}$$

$$A_\rho{}' = A_\rho + \sum_{j=1}^{\rho-1} \alpha_j A_j \tag{35.2}$$

It readily verified that these equations of transformation leave P invariant. We now suppose that eq. 30 are written in the directions which make

$$v_j > 0, j = 1\ldots\rho \tag{36}$$

This choice, in conjunction with ineq. 31.1 and 31.2, implies

$$A_j < 0, j = 1\ldots\tau \tag{37.1}$$
$$A_j > 0, j = \tau + 1\ldots\rho \tag{37.2}$$

Equation 35.1 and ineq. 37.1 imply

$$A_j{}' < 0, j = 1\ldots\tau \tag{38}$$

Hence for the first τ members of the desired set of inequalities (33.1) to hold, it is necessary and sufficient that

$$v_j{}' < 0, j = 1\ldots\tau \tag{39}$$

This condition, by virtue of eq. 34.1 and ineq. 36, is seen to be equivalent to

$$\alpha_j > \frac{v_j}{v_\rho}, j = 1\ldots\tau \tag{40}$$

Equation 35.1 and ineq. 37.2 imply

$$A_j{}' > 0, j = \tau + 1\ldots\rho - 1 \tag{41}$$

Hence for members no. $\tau + 1$ to $\rho - 1$ inclusive of the desired set of inequalities 33.1 to hold, it is necessary and sufficient that

$$v_j{}' > 0, j = \tau + 1 \ldots \rho - 1 \tag{42}$$

This condition, by virtue of eq. 34.1 and ineq. 36, is seen to be equivalent to

$$\frac{v_j}{v_\rho} > \alpha_j, j = \tau + 1\ldots\rho - 1 \tag{43}$$

(9) In the language of linear transformation theory this proposition may be stated as follows: it is always possible to transform the set (30) with coupling into a set without, by a matrix of the form

$$\begin{pmatrix} 1 & 0 & \cdots & 0 & \alpha_1 \\ 0 & 1 & \cdots & 0 & \alpha_2 \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & \cdots & 1 & \alpha_{\rho-1} \\ 0 & 0 & \cdots & 0 & 1 \end{pmatrix}$$

Equation 34.2 and ineq. 36 imply

$$v_\rho' > 0 \qquad (44)$$

Hence for the ρ'th member of the desired set of inequalities 33.1 to hold, it is necessary and sufficient that

$$A_\rho' > 0 \qquad (45)^{[10]}$$

We shall show later that for ineq. 45 to hold, the following conditions on the α_j are sufficient though not necessary

$$\frac{v_j}{v_\rho} + \frac{C}{|A_j|} > \alpha_j, j = 1\ldots\tau \qquad (46.1)$$

$$\alpha_j > \frac{v_j}{v_\rho} - \frac{C}{A_j}, j = \tau + 1\ldots\rho - 1 \qquad (46.2)$$

where C is defined by

$$C = \frac{P}{(\rho - 1)v_\rho} \qquad (47)$$

Accepting this result for the present, we note that, owing to ineq. 31.3 and 36

$$C > 0 \qquad (48)$$

whence

$$\frac{C}{|A_j|} > 0, j = 1\ldots\tau \qquad (49)$$

and furthermore, owing to ineq. 37.2

$$\frac{C}{A_j} > 0, j = \tau + 1\ldots\rho - 1 \qquad (50)$$

It follows from ineq. 49 that ineq. 40 and 46.1 can hold simultaneously and from ineq. 50 that ineq. 43 and 46.2 can hold simultaneously. Thus the α_j will produce the desired transformation if they lie in the ranges

$$\frac{v_j}{v_\rho} + \frac{C}{|A_j|} > \alpha_j > \frac{v_j}{v_\rho}, j = 1\ldots\tau \qquad (51.1)$$

$$\frac{v_j}{v_\rho} > \alpha_j > \frac{v_j}{v_\rho} - \frac{C}{A_j}, j = \tau + 1\ldots\rho - 1 \qquad (51.2)$$

and this condition can always be met. It remains only to show that ineq. (46.1) and (46.2) constitute a sufficient but not necessary condition for ineq. 45. By virtue of ineq. 37.1 and 37.2 and a few obvious rearrangements, we transcribe ineq. 46.1 and 46.2 to the single statement

$$C - \frac{1}{v_\rho} A_j (v_j - \alpha_j v_\rho) > 0, j = 1\ldots\rho - 1 \qquad (52)$$

From this we deduce by summation

$$(\rho - 1)C - \frac{1}{v_\rho} \sum_{j=1}^{\rho-1} A_j(v_j - \alpha_j v_\rho) > 0 \qquad (53)$$

By virtue of eq. 47, 34.1, 34.2 and 35.1 this becomes

$$\frac{1}{v_\rho'} \left(P - \sum_{j=1}^{\rho-1} A_j'v_j' \right) > 0 \qquad (54)$$

But the left side of this inequality is seen by eq. 33.2 to be equal to A_ρ'. Hence ineq. 46.1 and 46.2 are a sufficient condition for ineq. 45. That they

(10) Our treatment of the general case, which up to this point has been completely parallel to that of the case $\rho = 2$, will now cease to be so, in that we shall for simplicity be content with a condition on the α_j, namely, ineq. 46.1 and 46.2, which will be seen to be sufficient for ineq. 45 but not necessary, whereas for the analogous ineq. 20 we readily found a condition on α, namely, ineq. 21, which is necessary and sufficient.

are not a necessary one follows from the obvious fact that ineq. 53 does not imply ineq. 52.

The converse of the proposition just proved is also true. We consider a set of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{ij}'Q_i = 0, j = 1\ldots\rho \qquad (55)$$

We suppose this set to be free of thermodynamic coupling; this means

$$A_j'v_j' > 0, j = 1\ldots\rho \qquad (56.1)$$

$$P = \sum_{j=1}^{\rho} A_j'v_j' > 0 \qquad (56.2)$$

It is then always possible to find a set of real numbers, $\alpha_1'\ldots\alpha_{\rho-1}'$, such that, of the equivalent set of reactions with the chemical equations

$$\sum_{i=1}^{\sigma} \nu_{ij}'Q_i = 0, j = 1\ldots\rho - 1 \qquad (57.1)$$

$$\sum_{i=1}^{\sigma} \left(\nu_{i\rho}' + \sum_{j=1}^{\rho-1} \alpha_j'\nu_{ij}' \right) Q_i = 0 \qquad (57.2)$$

the first τ members are coupled to the remaining $\rho - \tau$; this means

$$A_jv_j < 0, j = 1\ldots\tau \qquad (58.1)$$
$$A_jv_j > 0, j = \tau + 1\ldots\rho \qquad (58.2)$$

$$P = \sum_{j=1}^{\rho} A_jv_j > 0 \qquad (58.3)$$

where the unprimed letters refer to the new set of reactions.

The proof of this proposition is so readily constructed from that of the preceding one that we shall omit it and state only the sufficient conditions on the $\alpha_j'(j = 1\ldots\rho - 1)$ to which it leads. We suppose eq. 55 to be written in the directions which make

$$v_j' < 0, j = 1\ldots\tau \qquad (59.1)$$
$$v_j' > 0, j = \tau + 1\ldots\rho \qquad (59.2)$$

We define C' by

$$C' = \frac{P}{(\rho - 1)v_\rho'} \qquad (60)$$

and then find that the α_j' will produce the desired transformation if

$$\alpha_j' < \frac{v_j'}{v_\rho'}, j = 1\ldots\tau \qquad (61.1)$$

$$\frac{v_j'}{v_\rho'} - \frac{C'}{A_j'} < \alpha_j' < \frac{v_j'}{v_\rho'}, j = \tau + 1\ldots\rho - 1 \qquad (61.2)$$

a condition which can always be met.

Conclusion.—It therefore appears that, in any case in which we know the values of dn_i/dt and μ_i ($i = 1\ldots\sigma$), we can confer or revoke thermodynamic coupling by properly choosing a set of net chemical reactions out of an infinity of permitted sets, which is to say, by a stroke of the pen. It follows that without a further criterion for choice out of this infinity, thermodynamic coupling is neither an essential feature of any special class of systems dead or alive, nor an explanation of anything. Thermodynamics, as already said, supplies no such criterion. If any exists, the only possible source would seem to be the theory of reaction mechanism. Thus without reference to the latter,

further concern with thermodynamic coupling would seem to be useless. Of what use it might be in conjunction with reaction mechanism remains an open question.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

The Mechanism of Benzene Chemisorption on a Supported Nickel Catalyst

BY J. A. SILVENT AND P. W. SELWOOD

A further study of benzene chemisorption on a nickel–kieselguhr catalyst by the low frequency a.c. permeameter magnetic method has shown, as previously reported, that the process takes place by the formation of approximately six bonds, up to a temperature of about 120°. This is assumed to mean flat, non-dissociative adsorption. At higher adsorption temperatures the number of bonds increases rapidly until at 200° substantially complete dissociation of the benzene molecule is achieved. These conclusions are supported by analysis of the saturated hydrocarbons obtained by flushing the adsorbed benzene with hydrogen and trapping the products. The conclusions are also confirmed by measuring the volume of hydrogen denied access to the surface by the presence of pre-adsorbed benzene, admitted to the catalyst at progressively higher temperatures.

Introduction

In an earlier investigation by the low frequency a.c. permeameter method,[1] it was shown that benzene chemisorbed on silica-supported nickel is taken up primarily by the formation of six bonds. This suggests associative adsorption with the plane of the ring parallel to the nickel surface, although various other interpretations are not excluded by the magnetic data alone.

The maximum temperature of adsorption, in the earlier work, was 150°. In the present work the observations are extended to 200°, at which temperature extensive dissociative adsorption may be expected, and the conclusions reached by the magnetic method are confirmed through the use of several other lines of investigation.

Experimental

Magnetization–volume isotherms were obtained as previously described.[1] All measurements were made on Universal Oil Products nickel–kieselguhr containing 52.8% of nickel. The reduction and evacuation of samples, together with purification of reagents have all been described.

Subsequent to several runs it was necessary to determine the products obtainable by flowing hydrogen over the adsorbent–adsorbate system. The hydrogenated products were selectively collected in cold traps for analysis in a mass spectrometer or, for some samples, by vapor phase chromatography. Conditions of adsorption and hydrogenation are given in connection with the data presented below.

In one series of experiments it was desired to estimate the area of nickel occupied by adsorbed benzene or its dissociation products. This was possible because benzene is not hydrogenated over nickel at −78°.[1] The procedure was to determine the pressure–volume isotherm for hydrogen over the catalyst at −78°. The hydrogen then was desorbed by evacuation at 360°, following which a measured quantity of benzene was admitted to the surface. The sample then was cooled to −78° and another pressure-volume isotherm for hydrogen was obtained. The benzene, or its dissociation products, was thus shown to deny access of hydrogen to part of the nickel surface. The extent to which this denial of access occurred was, of course, a measure of the dissociative process which had occurred during chemisorption of the benzene. These experiments were performed over a considerable range of benzene adsorption temperatures.

In one experiment the benzene was adsorbed at a lower temperature, then heated, then cooled again to determine whether dissociative adsorption occurs primarily during the adsorption step or whether it may occur in a pre-adsorbed intact molecule if the temperature is raised.

Results

Magnetization–volume isotherms for benzene on nickel are shown in Fig. 1. It previously has been shown[2] that the isotherms for hydrogen have a slope which is somewhat dependent on temperature even at temperatures well above those at which appreciable physical adsorption may take place. This effect seems to be related to the range of nickel particle diameters present in any catalyst sample. Whatever may be the reason for this behavior it is clearly necessary to compare the isotherm slope of any adsorbate with that of hydrogen at the same temperature, if accurate determination of the number of surface bonds per molecule adsorbed is required. Isotherms for hydrogen are, therefore, shown in Fig. 2. It will be noted that the slopes for benzene rise much more rapidly with increasing temperature of adsorption than do those of hydrogen.

Table I shows the effect of pre-adsorbed benzene on the volume of hydrogen which may be adsorbed by the nickel at −78° up to a pressure of 1 atm. The data are presented as (1) temperature at which benzene was admitted to the surface, (2) volume (s.c.) of benzene vapor adsorbed per g. of nickel, (3) volume of hydrogen (s.c.) adsorbed per g. of nickel at −78°, (4) volume of hydrogen (s.c.) denied access to the nickel and (5) molecules of hydrogen denied access to the nickel per molecule of benzene vapor adsorbed.

Another result, which we believe to be of significance, is that in every case represented in Table I the slope of the magnetization–volume isotherm for hydrogen on a surface covered in part by benzene was the same as that on a bare nickel surface. This was true in spite of the fact that the total volume of hydrogen which could be taken up by the nickel was diminished substantially by the presence of pre-adsorbed benzene.

It is well known that adsorbed hydrocarbon molecules and their dissociation products are often quite difficult to remove by hydrogenation *in situ*. In spite of this enough product was obtained to confirm the conclusions reached on the basis of the

(1) P. W. Selwood, THIS JOURNAL, **79**, 4637 (1957).

(2) P. W. Selwood, *ibid.*, **78**, 3893 (1956).