match no.1 pp. 83-119 1975

ON THE KINETIC DETECTION OF SHORT LIVED INTERMEDIATES IN COUPLED SETS OF FIRST ORDER INTERCONVERSIONS AND ON THE DETERMINATION OF THE REACTION CONSTANTS BELONGING TO THE RESULTING MECHANISTIC SCHEMES.

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Abstract

In systems of n species interconverting by first order or pseudo first order reactions, the mutual dependences, caused by the Principle of detailed balancing, among the phenomenological reaction constants k_{phen}, the ratios of k_{phen} of equal origin, R_{phen}

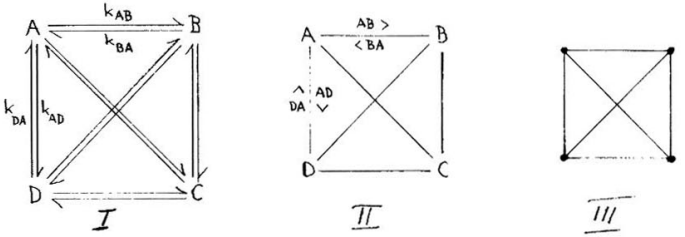
$$\left(= \frac{k_{CA}}{k_{CB}} \qquad = \left(\frac{dA}{dB}\right)_{\text{from C}} \qquad \equiv \left(\frac{A}{B}\right)_C \right)$$

and the ratios of R_{phen} of the type $\left(\frac{A}{B}\right)_C$ / $\left(\frac{A}{B}\right)_D$, here called T, are investigated and some relationships given. Then mechanistic schemes involving common reaction intermediates are introduced. To these mechanistic schemes belong the mechanistic reaction constants k_{mech} and the ratios of k_{mech} of equal origin, R_{mech}. (A particular mechanistic scheme may require of the T to have the value = 1. This may be used to decide whether this scheme is acceptable for a

particular system whose k_{phen} -values are known.) Criteria are then given by which one can tell whether or not all R_{mech} of a mechanistic scheme are calculable from the R_{phen} (which are accessible experimentally)and this is the aim of this paper. If, e.g., the mechanistic scheme, taken as a graph, represents a tree it is found that all R_{mech} are always calculable. If the graph contains cycles then the necessary and sufficent criterion for calculability is $u' + y = n(n - 1)/2 - e'$ where u' = number of independent T which are = 1 as required by the mechanistic scheme, y = number of independent R_{phen} made dependent by the mechanistic scheme in a way other than via T = 1, n = number of interconverting reactants, e' = number of the edges of the mechanistic graph. Since an easy procedure to enumerate u' is given and since y, as a rule, mostly = 0 (which however, can be checked by an other criterion, viz. (27)), this criterion should be easily applicable. If calculability has thus been shown, derivation of the equations which link the R_{mech} to the R_{phen} is rather straightforward for simple cases, making use of the quasistationarity of the reaction intermediates included in the mechanistic scheme.

I.) Phenomenological reaction schemes

Assume a system of n reactants where each reactant converts into every other one by first order or pseudo first reactions. For n = 4, e.g., this system would be described by reaction scheme I.



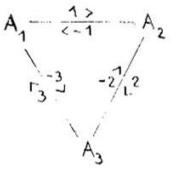
Let us call I the "phenomenological" reaction scheme (phenomenological since no assumptions regarding reaction intermediates are included) and k_{AB}, k_{DA}, etc. the phenomenological first order reaction constants k_{phen}.[1] No symmetries are assumed, i.e. the k_{phen} are in principle all different. II be a shorthand notation of I. III is the corresponding phenomenological reaction graph G^4_{phen}; for n reactants: G^n_{phen}; it is a complete graph because of our assumption that every reactant should convert into every other one.

II.) The effect of the Principle of detailed balancing.

The number of all k_{phen} in one n-reactant system = twice the number of all edges in $G^n_{phen} \equiv p$.

$$p = n(n - 1)$$

In every cycle any one k_{phen} is determined by all the other k_{phen} of that cycle by operation of the Principle of detailed balancing (PDB)[2] : e.g., for a three-membered cycle:



$$\text{PDB} \Longrightarrow \frac{k_1}{k_{-1}} = \frac{k_{-2}k_{-3}}{k_2\,k_3} \quad \text{so that}$$

$$\frac{k_1\,k_2\,k_3}{k_{-1}k_{-2}k_{-3}} = 1 \qquad (1)$$

generally, for a l-membered cycle:

$$\prod_{j=1}^{l} \frac{k_j}{k_{-j}} = 1 \qquad (1a)$$

Let us consider the p k_{phen} of G^n_{phen} one after the other in a deliberate sequence. Let us then call a k_{phen} which is PDB - independent from k_{phen} considered before a k^u_{phen} and the number of the k^u_{phen} of G^n_{phen} q; then

$$q = \frac{n(n+1)}{2} - 1 \qquad (2)$$

(Enumeration: In any tree containing n vertices (= a partial graph of G^n_{phen}) every edge (there are n - 1) will supply two k^u_{phen}, all the other edges which add up to G^n_{phen} (there are $\frac{n(n-3)}{2} + 1$) close cycles and therefore supply one k^u_{phen} each).

$\frac{k_{CA}}{k_{CB}} \equiv \left(\frac{A}{B}\right)_C$ = a ratio of k_{phen} of equal origin (in this case C) ≡ a R_{phen}

If $\left(\frac{A}{B}\right)_C$ and $\left(\frac{A}{D}\right)_C$ are given, then also $\left(\frac{B}{D}\right)_C$ is given: $\left(\frac{B}{D}\right)_C$ is implicitly dependent on $\left(\frac{A}{B}\right)_C$ and $\left(\frac{A}{D}\right)_C$. Let us call a R_{phen} which is implicitly independent from R_{phen} considered before a R^u_{phen} and the number of the R^u_{phen} of G^n_{phen} r; then

$$r = p - n = n(n-2)$$

Because of (1), (1a), i.e. by operation of PDB, in every cycle any one R_{phen} is determined by all the other R_{phen} of that cycle; e.g. from (1):

$$\frac{k_1}{k_{-3}} = \frac{k_{-2}}{k_3} \cdot \frac{k_{-1}}{k_2}$$

Let us call a R^u_{phen} which is PDB-independent from R^u_{phen} considered before and from the R_{phen} which depend on them (implicitly or by PDB) a R^{uu}_{phen} and the number of the R^{uu}_{phen} of G^n_{phen} s; then

$$s = \frac{n(n-1)}{2} - 1 \qquad (3)$$

Enumeration: Any tree containing n vertices (= a partial graph of G^n_{phen}) will supply n - 2 R^{uu}_{phen}; any further edge to add up to G^n_{phen} will close a cycle and supply one more R^{uu}_{phen}. It is thus seen that s equals the number of edges in G^n_{phen} minus one, and it is seen generally that with every edge in a G^n (which may be any reaction graph, not only the complete graph G^n_{phen}) but for the first one one R^{uu} is introduced. In other words: A one - to - one mapping can be made between the set of the edges diminished by one of a reaction graph and the set of its R^{uu}. (3a)

From what was said up to now one obtains

$$p - q = r - s = \frac{n(n-3)}{2} + 1 = c \qquad (4)$$

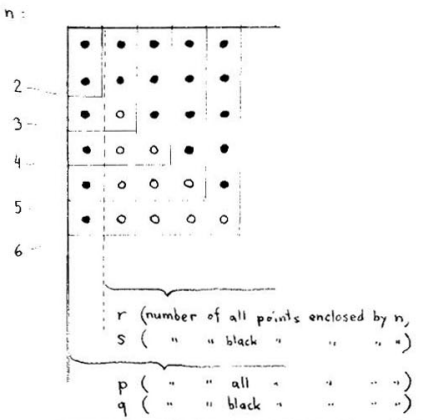
i.e., the number of PDB-dependent k_{phen} equals the number of PDB-dependent R^u_{phen}; both equal the number of independent cycles (i.e. cycles which are not generated by cycles considered before) in G^n_{phen} which is denoted by c.

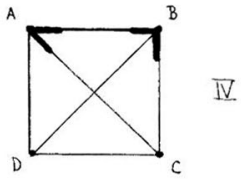
For a convenient synopsis relating p,q,r and s see below.

Easy graphical procedure to choose a set of R^{uu}_{phen}: (5)
The R^{uu}_{phen} are chosen deliberately except for the following restrictions: Every chosen R^{uu}_{phen} is introduced into G^n_{phen} in fat print, e.g. $\left(\frac{B}{C}\right)_A$ and $\left(\frac{A}{C}\right)_B$ in Scheme IV. Two R_{phen} on the same center which have in common one branch (Scheme V) generate a third R_{phen} comprising the other two branches. Whereever only one more R_{phen} is required to complete a cycle (e.g. $\left(\frac{A}{B}\right)_C$ in scheme IV) this R_{phen} is also introduced in fat print before continuing to choose another

R^{uu}_{phen}. All R_{phen} generated and introduced that way are no longer eligible as R^{uu}_{phen}.

Synopsis of p,q,r,s:



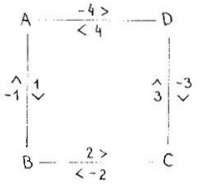


Comment: If in a system of n interconverting reactants one has already determined the product ratios R^{u}_{phen} of j - 1 reactants, then of the n - 2 R^{u}_{phen} of the j^{th} reactant j - 2 are determined by PDB and thus predictable. Thus of the n^{th} (the last) reactant all product ratios are predictable.

If, on the other hand, in that system all k_{phen} or R^{u}_{phen} have been determined, of these only n(n + 1)/2 - 1 or n(n - 1)/2 - 1, respectively, will yield real information on the system, the residual n(n - 3)/2 + 1 k_{phen} or R^{u}_{phen} merely informing about the validity of PDB and/or the experimental accuracy [3].

III.) The T

Let us consider a four-cycle within G^{n}_{phen}:



From (1a) we see: $\frac{k_{-1}k_{-3}}{k_2\ k_4} = \frac{k_1\ k_3}{k_{-2}k_{-4}}$

i.e. : $\frac{\left(\frac{A}{C}\right)_B}{\left(\frac{A}{C}\right)_D} = \frac{\left(\frac{B}{D}\right)_A}{\left(\frac{B}{D}\right)_C}$ (6)

Let us call $\left(\frac{A}{C}\right)_B / \left(\frac{A}{C}\right)_D \left(= \frac{k_{-1}k_{-3}}{k_2\ k_4}\right)$ or $\left(\frac{B}{D}\right)_A / \left(\frac{B}{D}\right)_C \left(= \frac{k_1 k_3}{k_{-2}k_{-4}}\right)$

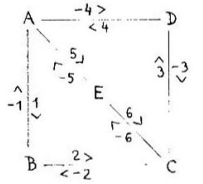
a T (7)

Every four-cycle contains one T and a second one which because of (6) equals the first one.

Dependences

between four-cycles:

a.)

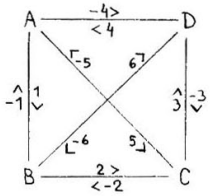


If the T of four-cycle (ABCD) is given $\left(= \frac{k_{-1}k_{-3}}{k_2\ k_4} = \frac{k_1\ k_3}{k_{-2}k_{-4}}\right)$ and that of the four-cycle (ABCE) $\left(= \frac{k_{-1}\ k_6}{k_2\ k_{-5}} = \frac{k_1\ k_{-6}}{k_{-2}\ k_5}\right)$ then the T of the third four-cycle (AECD) $\left(= \frac{k_{-5}k_{-3}}{k_6\ k_4} = \frac{k_5\ k_3}{k_{-6}k_{-4}}\right)$

is determined by the other two T:

$$\frac{k_{-1}k_{-3}}{k_2\,k_4} \cdot \frac{k_2k_{-5}}{k_{-1}k_6} = \frac{k_{-5}k_{-3}}{k_6\,k_4}\,, \text{ i.e. } T_3 = \frac{T_1}{T_2} \qquad (8)$$

b.) The same is found for the three four-cycles (ABCD), (ACBD) and (ABDC):



$$\frac{k_{-1}k_{-3}}{k_2\,k_4} \cdot \frac{k_2k_{-4}}{k_6k_5} = \frac{k_{-1}k_{-3}k_{-4}}{k_6\,k_4\,k_5}\,;$$

because of (1): $\dfrac{k_{-3}k_{-4}}{k_4\,k_5} = \dfrac{k_3}{k_{-5}}$

hence: $\dfrac{k_{-1}k_{-3}}{k_2\,k_4} \cdot \dfrac{k_2k_{-4}}{k_6\,k_5} = \dfrac{k_{-1}k_3}{k_6k_{-5}}$ (8a)

i.e. $T_1 \cdot T_2 = T_3$

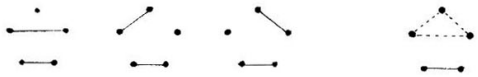
Thus if three four-cycles are coupled according to a.) or b.), then of the three T any one is determined by the other two according to (8) or (8a), respectively.

Easy graphical procedure to detect dependences according to a.) or b.): (9)

ad. a.) Three coupled four-cycles:

dependence rule:

represented as:



ad. b.) Three coupled four-cycles:  dependence rule:

represented as: 

Let us call a four-cycle and its T dependent if its T is determined by the T of four-cycles considered before and independent if this is not so. Let us denote a T of an independent four-cycle by T^u.

c.) A four-cycle will always be independent if it contains at least one edge not belonging to any four-cycle considered before.

This is so because this edge contains a pair of k_{phen} which cannot be contained in any T of four-cycles considered before and this, as is easily seen from (7), will make that T, i.e. that four-cyle, independent.

It can be shown that[2]:

1.) A four-cyle is dependent if and only if it depends by couplings a.) and/or b.) and will be independent otherwise. (10)

From (10) follows: Procedure to choose a set of T^u: (11)

From the set of the $3\binom{n}{4}$ T one T^u after the other is choosen deliberately and after each single choice those T which depend (from T^u already chosen or from T already found dependent) according to couplings a.) and/or b.) are detected (most easily graphically by means of (9)) and set aside, before continuing to choose.

2. See "proofs and demonstrations"

2.) The number t of the independent four-cycles or T^u in G^n_{phen} equals to

$$t = \frac{n(n-3)}{2} \qquad (12)$$

$$= c - 1$$

(the total of all four-cyles in $G^n_{phen} = 3\binom{n}{4}$)

3.) For any given set of T^u it is always possible to map to each T^u one R^{uu}_{phen} contained in it (every T is a ratio or a product of two R_{phen}, so we say: it contains two R_{phen}). (13)

Because of (3a) this can also be stated in the form: In every set of independent four-cycles, to each independent four-cycle one edge contained in it can be mapped. Or: Every independent four-cycle is so because of c.)

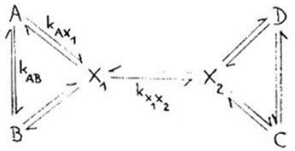
Furthermore one can see: If a subset of the T in G^n_{phen}, whose elements be denoted by T', is complete in the sense that every T dependent from two T' by couplings a.) or b.) is also a T', then the total number of the T'^u (= T^u of this subset) must be independent from the mode of choice and therefore characteristic for this subset. (Example: The $3\binom{m}{4}$ T in $G^m_{phen} \subset G^n_{phen}$ (m< n) form such a subset, the number of T'^u being m(m -3)/2).
In a particular system with known numerical values of the R_{phen}, those T which = 1 (such T be denoted $_1T$) form a subset of the T complete in the above mentioned sense: a T depending on two $_1T$ by couplings a.) or b.) can only be another $_1T$ (cf.(8),(8a)). Therefore, the number of the $_1T^u$ (= T^u of this subset) must be inde-

pendent from the mode of choice and characteristic for this subset, and therefore, characteristic for that particular system.

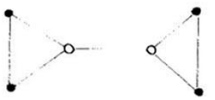
Number of the ${}_1T^u$ in a particular system $\equiv u$. $u \leq t$ (14)

The ${}_1T^u$ may be chosen from the set of the ${}_1T$ by (11).

IV.) Mechanistic reaction schemes



VI



VII

VI = one of many possible mechanistic reaction schemes for n = 4

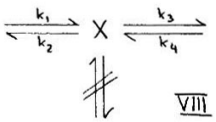
VII = the corresponding mechanistic reaction graph G^4_{mech}

X_1, X_2 = intermediate reaction stages which 1.) have negligibly small quasistationary concentrations and 2.) are reaction branching points.[1]

k_{AB}, k_{AX_1}, $k_{X_1X_2}$ = mechanistic reaction constants k_{mech}. They are assumed to be first order or pseudo first order.

A G^n_{mech} must have between every pair of reactants (say A, B) at least one connection which either runs directly or via X but not via other reactants (15). To every n-component system corresponds only one G^n_{phen} but in principle an infinite number of G^n_{mech}.

1. The k_{mech} and R_{mech} involved with an X which were no branching point could not be determined (as long as we are dealing with first order or pseudo first order reactions!) because the arrangement VIII in a mechanistic scheme is always replaceable by the arrangement IX (with $k_5 = k_1k_3 / (k_2 + k_3)$ and $k_6 = k_2k_4 / (k_2 + k_3)$) without any effect on the k_{phen}



VIII

IX

Therefore such nonbranching intermediates are dropped from the mechanistic reaction schemes, the k_{mech} being in principle "compound" reaction constants like k_5 and k_6 mentioned above.

In analogy to the R^{uu}_{phen} in the phenomenological reaction scheme, in the mechanistic reaction scheme we have the R^{uu}_{mech} whose number be denoted by s'. From (3a) follows

$$s' = e' - 1 \qquad (16) \qquad e' = \text{number of edges in } G^n_{mech}$$

$$= \frac{p'}{2} - 1 \qquad p' = \text{number of the } k_{mech}$$

A G^n_{mech} may imply ${}_1T$. E.g., VII (or VI) implies the following ${}_1T$:

$$\frac{\left(\frac{A}{B}\right)_C}{\left(\frac{A}{B}\right)_D} = 1 \quad \Longleftrightarrow \quad \text{because of (6)} \quad \Longleftrightarrow \quad \frac{\left(\frac{C}{D}\right)_A}{\left(\frac{C}{D}\right)_B} = 1$$

We note generally: G^n_{mech} will imply a ${}_1T$, say $\left(\frac{A}{B}\right)_C / \left(\frac{A}{B}\right)_D = 1$, whenever and only when there is at least one X through which all connections in G^n_{mech} from A to C, A to D, B to C and B to D run. (17)

Using this criterion we can in a straightforward manner find the set of ${}_1T$ implied by a G^n_{mech}. From this set of implied ${}_1T$ we can choose a set of implied ${}_1T^u$ by means of (11).

A G^n_{mech} is acceptable for a particular n-component system if all ${}_1T^u$ which it implies have been verified experimentally.

The number of ${}_1T^u$ implied by $G^n_{mech} \equiv u'$. Always $u' \leqslant t = \frac{n(n-3)}{2}$ (18)

If G^n_{mech} is acceptable then also $u' \leqslant u$

From (13) follows that for every ${}_1T^u$ implied by G^n_{mech} the R^{uu}_{phen} contained in and mapped to that ${}_1T^u$ is made equal by G^n_{mech} to the

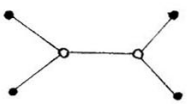
second R_{phen} contained in that ${}_1T^u$ and is thus determined by the second R_{phen}. So of the $n(n-1)/2 - 1$ R^{uu}_{phen}, u' are made dependent by G^n_{mech} via implied ${}_1T^u$ from the remaining $n(n-1)/2 - 1 - u'$ R^{uu}_{phen}. There may be implications other than via ${}_1T^u$ by which G^n_{mech} makes R^{uu}_{phen} dependent from others; the number of such extra implications $\equiv y$.

Let us call a R^{uu}_{phen} which is not made dependent by G^n_{mech} from R^{uu}_{phen} considered before a R^{uuu}_{phen} and the number of R^{uuu}_{phen} for a particular G^n_{mech} v; then according to what was said

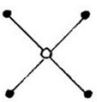
$$v = s - u' - y = \frac{n(n-1)}{2} - u' - y - 1 \qquad (19)$$

Developing G^n_{mech} from G^n_{phen}:

If a G^4_{phen} (= partial graph of G^n_{phen} for a particular n-reactant system) contains one ${}_1T^u$ which one would like to consider as implied rather than accidental, then it has to be replaced by a G^4_{mech} in compliance with (17). Of an infinite number of G^4_{mech} complying with (17) a simple one would be X.



X



XI

If G^4_{phen} contained two ${}_1T^u$ (it can contain no more than two T^u) which one would consider as implied then it can be shown that a.) there is then only one G^4_{mech} complying with (17), viz. XI, b.) one may consider the two ${}_1T^u$ only as either both implied or both

accidental. (20)

We note that in X all six edges of G^4_{phen} have been replaced (Four of them had to in order to comply with (17); the residual two could since they no longer represented the only connections between their respective reactants).

If two G^4_{phen} each containing at least one ${}_1T^u$ (such G^4_{phen} we denote by ${}_1G^4_{phen}$) share at least one edge we say they are linked together. If a third ${}_1G^4_{phen}$ shares at least one edge with at least one of these two ${}_1G^4_{phen}$ we say all three are linked together. If some ${}_1G^4_{phen}$ are linked together we call these a completed set of linked ${}_1G^4_{phen}$ if none of them is linked to another ${}_1G^4_{phen}$ not belonging to that set. Let us call those l ($n \geqslant l \geqslant 4$) vertices (reactants) which take part in a completed set of linked ${}_1G^4_{phen}$ a mechanistic subsystem of the n-reactant system. Then we can generalize what we had said before for l = 4 :

The G^l_{phen} (= a partial graph of G^n_{phen}) corresponding to a mechanistic subsystem of l reactants out of the n has to be replaced by a G^l_{mech} which has to be acceptable as judged by criteria (15) and (17) and which will not (because the ${}_1G^4_{phen}$ partaking in the subsystem are linked) be separable into independent sub-G_{mech}. (21)

Those edges (and their two k_{phen}) in G^n_{phen} which do not take part in any ${}_1G^4_{phen}$ are left untouched by this procedure. (Even inside a G^l_{mech}, some of the edges (and their two k_{phen}) of G^n_{phen} may remain untouched.) This means that from the standpoint of the ${}_1T^u$ there is no need to change the mode of connection and hence the two k_{phen} between a pair of reactants not belonging to a mechanistic subsystem - although of course one is free to do so if one has chemical reasons for it.

A mechanistic subsystem of l reactants thus can be considered

completely by itself without considering the residual n - 1 reactants. Therefore, all what we are going to say in the following will be about mechanistic subsystems only; for continuity, instead of the index 1 the index n will be used further. (21a)

For most conceivable combinations of ${}_1T^u$ there are also acceptable G^n_{mech}. This means that mostly the set of ${}_1T^u$ contains no redundancy as fas as information on the structure of G^n_{mech} is concerned, every ${}_1T^u$ supplying an independent information on G^n_{mech}. If however for a certain set of ${}_1T^u$ there exists no acceptable G^n_{mech}, than that or those ${}_1T^u$ must be accidental which one has to drop in order to obtain an acceptable G^n_{mech} for the residual set of ${}_1T^u$. One example is provided by the following set of ${}_1T^u$ for n = 6:

Here the ${}_1T^u$ to the right has to be taken as accidental.

V.) the relation between the ratios of mechanistic reaction constants R^{uu}_{mech} and the ratios of phenomenological reaction constants R^{uu}_{phen}.

It can be shown[2]:

For a n-component system and any given G^n_{mech}, the values of all R^{uu}_{phen} are determined by, and only by, those of all R^{uu}_{mech}. (22)

From (22) follows: The number of the R^{uuu}_{phen} cannot exceed that of the R^{uu}_{mech}:

$$s' \geqslant v \tag{23}$$

From this and (16) and (19) follows

$$u' + y \geq s - s' = \frac{n(n-1)}{2} - e' \qquad (23a)$$

which says: a G^n_{mech} makes at least as many R^{uu}_{phen} dependent from others as it has less edges than G^n_{phen}.

Since $e' = n + x + c' - 1$, where $x \equiv$ number of branching points X

$c' \equiv$ number of independent cycles in G^n_{mech} (analogous to c for G^n_{phen})

we have

$$u' + y \geq \frac{n(n-3)}{2} - x - c' + 1 \qquad (23b)$$

this with (12) gives

$$u' + y \geq t - x - c' + 1 \qquad (23c)$$

$$u' + y \geq c - c' - x \qquad (23d)$$

Relations (23x) hold for all G_{mech}.

Now we can set out towards our goal and answer the question whether we can determine all R^{uu}_{mech} from the R^{uuu}_{phen} (which are accessible experimentally).

Necessary for all R^{uu}_{mech} to be determined from the R^{uuu}_{phen} (we say: for G^n_{mech} to be "calculable") would be: $v \geq s'$; since (23) holds, this reduces to

$$v = s' \qquad (24)$$

As the system of equations linking the R^{uuu}_{phen} to the R^{uu}_{mech} is not separable into independent subsystems (which follows from (21) and (21a) since we are considering a mechanistic subsystem of reactants and since the G^{n}_{mech} of such a one is not separable into independent sub-G_{mech}) it follows that (24) is also sufficient. Thus we can state:

(24) is necessary and sufficient for a G^{n}_{mech} of a mechanistic subsystem to be "calulable".

Comparison of (24) and (23) and keeping in mind (16) shows:

Only those G^{n}_{mech} are "calculable" which for a given v (i.e., for a given u' + y) have the minimum number of edges. (24e)

In analogy to (23a - d) condition (24) can be written:

$$u' + y = \frac{n(n-1)}{2} - e' \qquad (24a)$$

$$= \frac{n(n-3)}{2} - x - c' + 1 \qquad (24b)$$

$$= t - x - c' + 1 \qquad (24c)$$

$$= c - c' - x \qquad (24d)$$

For a particular G^{n}_{mech}, all the above quantities except y are easily enumerated. Unfortunately y is not readily evaluated and this presents a problem. To circumvent the problem one has, however, the following possiblities:

1.) The necessary and sufficient condition (24x) contains the necessary condition

$$u' \leq \frac{n(n-1)}{2} - e' \qquad (25a)$$

(25b - d) in analogy to (24b - d)

2.) Rule (not proven!) : (26)

It appears that for a mechanistic subsystem (cf. (21), (21a)) always $y = 0$ except when $s - u' > s'$: then $y = s - s' - u'$ (which is just condition (24) so that it means at the same time that a G^n_{mech} with $y > 0$ is always calculable)

3.) Sufficient condition for calculability[2]: (27)

If a G^n_{mech} contains only such edges whose cancellation would either interrupt the only connection between any pair of reactants or would imply a new ${}_1T^u$, and/or such edges between two X, whose elimination by merging the two X would imply a new ${}_1T^u$, then it is calculable.

4.) It can be shown[2]:

a.) If G^n_{mech} is a tree it is always calculable. (28)

b.) If G^n_{mech} is a tree then always $y = 0$ (29)

From (28) and (29) together with (24) follows further that for a tree

$$u' = \frac{n(n-3)}{2} - x + 1$$
$$= t - x + 1$$
$$= c - x$$

Comments:

1.) The R^{uu}_{mech} which is indicated by fat print in XII will always be calculable and simply = $\left(\frac{A}{B}\right)_J$ even if the rest of G^n_{mech} is not calculable. (30)

2.) Since for a particular set of ${}_1T^u$ in general there is an infinite set of acceptable G^n_{mech} with only few of them having the minimum number of edges and thus being calculable (see (24e)) and since the ones with the minimum number will not always be those which are the most reasonable ones from a chemical point of view there may frequently be a conflict between calculability and reasonableness of a G^n_{mech}. A remedy might then be to assume a relationship which expresses one R^{uu}_{mech} by others and thus to decrease the effective number of R^{uu}_{mech} and make the reasonable G^n_{mech} calculable.

3.) If the n-reactant system contains symmetries, i.e. if some reactants have equal k_{phen} and R_{phen} because they are optical antipodes or isotopic isomers then they also have equal k_{mech} and R_{mech} and there will be a symmetrical G^n_{mech} . To assess calculability

one then has to find the effective number of edges in G^n_{phen} and G^n_{mech} (and likewise the effective number of R^{uuu}_{phen} and R^{uu}_{mech}) by eliminating those edges and R which are generated from others by symmetry operations, within the G^n_{mech} and the G^n_{phen}.

4.) Calculability of a G^n_{mech} does not mean that from real positive values of R^{uuu}_{phen} there will always result real positive values of R^{uu}_{mech}. If they don't then this G^n_{mech} is falsified for that particular reactant system[3].

5.) The concept may be extended to systems with reactions of higher order. One may keep the concentrations of reactants known and constant (or nearly constant) during experimental determination of the k_{phen} and may thus use them as parameters with which to define pseudo first order k_{phen} and k_{mech} from the higher order reaction constants. With all reaction constants being made pseudo first order in this way any system is amenable to the present treatment.

Moreover, the calculability situation is highly improved in such systems: G^n_{mech} become calculable even though they contain more R^{uu}_{mech} than there are R^{uuu}_{phen}. This is because the variation of the R^{uuu}_{phen} with the concentration of a reactant can be measured and yields additional information; it is given as a function of the R^{uu}_{mech} by differentiating the equation expressing the R^{uuu}_{phen} by the R^{uu}_{mech} with respect to the reactant concentration. Thus the set of equations which to transform into the set of equations expressing the R^{uu}_{mech} by experimental values is increased. A general discussion of all possibilities which then exist would, however, blow up the scope of this paper and can be omitted since the reader probably will have no difficulties in working out the special cases he is interested

in.

3. A fine example is found in the work of Doering [4] :
The (symmetrical) calculable G^4_{mech} on p.1178 leads for one particular R^{uu}_{mech} to the expression (in the authors' notation) :

$$\left(\frac{r}{Ar}\right) = \left[\frac{\left(\frac{T}{\mathcal{C}}\right)_C - \left(\frac{T}{\mathcal{C}}\right)_\tau}{\left(\frac{C}{\mathcal{C}}\right)^2_\tau \left(\frac{T}{\mathcal{C}}\right)_C - \left(\frac{T}{\mathcal{C}}\right)_\tau}\right]^{\frac{1}{2}}$$

Upon inserion of the authors' experimental values an imaginary value for $\left(\frac{r}{Ar}\right)$ results. (The same conclusion, i.e. that this G^4_{mech} is unacceptable for the system studied, has been reached by the authors via a different route of reasoning.)

VI.) Derivation of the expressions for the R^{uu}_{mech} :

1.) Equations which express the ${}_{A}R^{uuu}_{phen}$ (R^{uuu}_{phen} of origin A) as a function of the R^{uu}_{mech} are obtained by starting from the x quasi-stationarity conditions for the X and assuming the concentration of all reactants except A to be zero. The same as for A is then done for the other reactants.

2.) The system of v(= s') equations thus obtained expressing the v R^{uuu}_{phen} by the v R^{uu}_{mech} is then transformed into the system of v equations expressing the v R^{uu}_{mech} by the v R^{uuu}_{phen}.

VII.) Possible procedure, starting out from experimentally determined k_{phen} or R_{phen}.

1.) Split the information given by k_{phen} (n(n - 1) experimentally determined values) into n(n - 2) R^{u}_{phen} and n k_{phen} of unequal origin.

2.) Find all ${}_{1}T$; choose the ${}_{1}T^{u}$ from the ${}_{1}T$ according to (11); decide which of the ${}_{1}T^{u}$ shall be considered as implied and which as accidental and at the same time choose that acceptable (in view to the ${}_{1}T^{u}$) G^{n}_{mech} which is the most reasonable one chemically (see: Developing G^{n}_{mech} from G^{n}_{phen}, p. 96 ff.)

3.) To every implied ${}_{1}T^{u}$ map one R^{uu}_{phen} contained in it (see (5), (13)), complete this subset of u' R^{uu}_{phen} to give the complete set of n(n -1)/2 - 1 R^{uu}_{phen} by choosing the residual R^{uu}_{phen} (which are the R^{uuu}_{phen}) using (5). Check the experimental accuracy and/or

validity of PDB by calculating the depending R^{u}_{phen} from the R^{uu}_{phen} by means of PDB (1a) and comparing with the experimental values.

4.) Check calculability of the chosen G^{n}_{mech} for every mechanistic subsystem (see (21) (21a)) according to p. 99 ff. If necessary, make it calculable (see 2.) p. 102).

5.) Derive the expressions which give the R^{uu}_{mech} as functions of the R^{uuu}_{phen} (see VI)

6.) Calculate the values of the R^{uu}_{mech} from those of the R^{uuu}_{phen} and check if they are real and positive otherwise the chosen G^{n}_{mech} would be falsified for that system.

7.) The ${}_{J}k_{mech}$ (k_{mech} whose origin is a reactant J) are then also calculable from the n k_{phen} of unequal origin (see 1.)), the R^{uu}_{phen} and the R^{uu}_{mech} by making use of the quasistationarity conditions for the X.

8.) Convert the R^{uu}_{mech} and ${}_{J}k_{mech}$ into energy- and entropy- information.

VIII.) Flow of information

$n(n-1)\ k_{phen}$ ——— > n k_{phen} of unequal origin: Energies and entropies of the reactants relative to each other and to the transition states.

$n(n-2)\ R^{u}_{phen}$ ⟶ $\frac{n(n-3)}{2} + 1$ dependent

R^{u}_{phen}: experimental accuracy and/or validity of PDB

$\frac{n(n-1)}{2} - 1\ R^{uu}_{phen}$ ⟶ $u' + y \leq \frac{n(n-3)}{2}\ R^{uu}_{phen}$

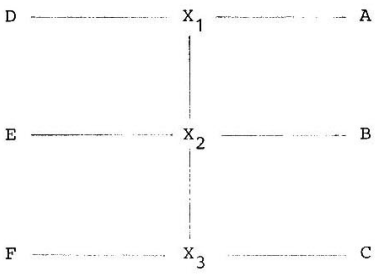
made dependent from other R^{uu}_{phen} by G^{n}_{mech}: Structure of G^{n}_{mech}

$\frac{n(n-1)}{2} - u' - y - 1$

$(\geq n-1)\ R^{uuu}_{phen}$:

R^{uu}_{mech} . ⟶ energies and entropies of the transition states corresponding to G^{n}_{mech} relative to each other

IX.) Example



For this tree there must be 7 R^{uuu}_{phen} (since v = s' = e' - 1 = 7) out of 14 R^{uu}_{phen} (so that there are 14 - 7 = 7 implied ${}_1T^{u}$ out of 9 T^{u}). Proceeding along VII 2.) 3.) these R^{uuu}_{phen} are chosen as, say:

$$\left(\frac{E}{B}\right)_A, \quad \left(\frac{D}{E}\right)_A, \quad \left(\frac{F}{E}\right)_A, \quad \left(\frac{F}{C}\right)_A, \quad \left(\frac{D}{A}\right)_B, \quad \left(\frac{D}{E}\right)_B, \quad \left(\frac{F}{E}\right)_C,$$

7 R^{uu}_{mech} are to be calculated from these 7 R^{uuu}_{phen}.
Three are obtained in a straightforward way (see (30)) :

$$\frac{k_{1D}}{k_{1A}} = \left(\frac{D}{A}\right)_B ; \quad \frac{k_{2E}}{k_{2B}} = \left(\frac{E}{B}\right)_A ; \quad \frac{k_{3F}}{k_{3C}} = \left(\frac{F}{C}\right)_A$$

For the residual four the following equations are derived:

$$\frac{k_{12}}{k_{1D}} = \frac{1+\left(\frac{B+C+F}{E}\right)_A + \left(\frac{A+D}{E}\right)_B}{\left(\frac{D}{E}\right)_A - \left(\frac{D}{E}\right)_B} = \frac{\left(\frac{B}{E}\right)_A - \left(\frac{B}{E}\right)_B}{\left(\frac{D}{E}\right)_A - \left(\frac{D}{E}\right)_B}$$

$$\frac{k_{32}}{k_{3F}} = \frac{1+\left(\frac{B+C+F}{E}\right)_A + \left(\frac{A+D}{E}\right)_B}{\left(\frac{F}{E}\right)_C - \left(\frac{F}{E}\right)_A} = \frac{\left(\frac{B}{E}\right)_A - \left(\frac{B}{E}\right)_B}{\left(\frac{F}{E}\right)_C - \left(\frac{F}{E}\right)_B}$$

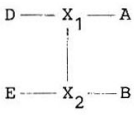
$$\frac{k_{21}}{k_{2E}} = \frac{\left(\frac{A}{D}\right)_B - \left(\frac{A}{D}\right)_A}{\left(\frac{E}{D}\right)_B - \left(\frac{E}{D}\right)_A}$$

$$\frac{k_{23}}{k_{2E}} = \frac{\left(\frac{C}{F}\right)_B - \left(\frac{C}{F}\right)_C}{\left(\frac{E}{F}\right)_B - \left(\frac{E}{F}\right)_C}$$

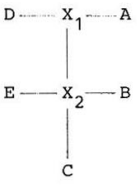
$$\left[\begin{array}{l} \left(\frac{C}{F}\right)_B = \left(\frac{C}{F}\right)_A ; \quad \left(\frac{E}{F}\right)_B = \left(\frac{E}{F}\right)_A \\ -\left(\frac{C}{F}\right)_C = 1 + \left(\frac{E}{F}\right)_C \left[1 + \left(\frac{A}{E}\right)_B + \left(\frac{B}{E}\right)_A + \left(\frac{D}{E}\right)_I \right. \end{array}\right.$$

We note that these equations can be expressed in different ways since one can replace the R^{uuu}_{phen} by other R_{phen} using implicit or PDB - or ${}_1T^u$ - dependence. It is a question of convenience which of the possible expressions to use.

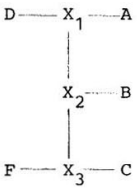
We note further that from these equations one can obtain the equations for sub-trees of the tree above such as XIII, XIV, XV.



XIII



XIV



XV

Obtaining these equations will in general involve replacement of the R^{uuu}_{phen} by other R_{phen} using the three types of denpendences (in order to remove dropped reactants from the equations) and keeping in mind footnote 1 (p.94). The equations for system XIII are obtained in a straightforward way:
The expressions for $\frac{k_{1D}}{k_{1A}}$, $\frac{k_{2E}}{k_{2B}}$, $\frac{k_{12}}{k_{1D}}$ (using the expression in brackets at the right) and $\frac{k_{21}}{k_{2E}}$ can be used directly as is clearly seen (They were however derived independently also); for $\frac{k_{12}}{k_{1D}}$ alternatively the left-hand expression may be used after cancellation of C and F. These expressions can be applied to particular systems XIII described in the literature to give an improved nonapproximative treatment instead of the approximate treatments given here.[5][6]4

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4 For the system studied by Bartlett[5], Z-butene(2), E-butene(2) and the two stereoisomeric cyclobutane adducts of these to tetrafluoroethylene, this makes a considerable difference: The R^{uu}_{mech} - values given in Scheme 1 of Bartlett's paper: 0,71; 0,23; 2,2; 0,5 are to be replaced by the values 0,149; 0,0495; 0,435; 0,106, respectively.

Proofs and demonstrations:

To see (10) and (12), let us consider all four-cyles in G^{n}_{phen} successively in such a way that each four-cycle considered shares as many vertices and edges as possible with four-cycles considered before. Then we will find that each four-cycle will either depend by couplings a.) and/or b.) or will be independent according to c.); at the same time we will verify (12). n(n -3)/2, in this particular procedure, is thus both the total of all T mutually independent in respect to couplings a.) and b.) and the total of all T^{u}, i.e. T mutually independent in respect to any coupling whatsoever. It will, of course, be possible to choose several different sets of T^{u} and to choose them by procedures different from that above. But whatever the choice, both totals, viz., the number of all T mutually independent in respect to couplings a.) and b.) and the number of all T^{u}, must remain the same, n(n - 3)/2. From this follows (10).

To see (13), let us take from any complete set of T^{u} (n(n - 3)/2 T^{u}) a subset of $1 < n(n - 3)/2$ T^{u}. We note that these 1 T^{u} are given by 2 1 R_{phen} where some of these R_{phen} may be identical. Since these 1 T^{u} are 1 quantities independent from each other, among the R_{phen} which give them there must be at least 1 which are independent from each other, i.e. at least 1 R^{uu}_{phen}. Now let us add another T^{u} to give a subset of 1 + 1 T^{u}. This subset must be given by at least 1 + 1 R^{uu}_{phen}. Now there are two possibilities: 1.) If the 1 T^{u} were given by exactly 1 R^{uu}_{phen} then the $(1 + 1)^{st}$ T^{u} must contain at least one <u>new</u> R^{uu}_{phen} so that for this T^{u} (13) is fulfilled. 2.) If the 1 T^{u} were given by more than 1 R^{uu}_{phen} then: 2a.) If the $(1 + 1)^{st}$ T^{u}

contains at least one new R^{uu}_{phen} then again (13) is fulfilled; 2b.) if it does not then: 2ba.) If it contains at least one R_{phen} which is either an "excess" R^{uu}_{phen} (if a T^u considered before contained two R^{uu}_{phen}, the second of these which one had not mapped to that T^u is called in "excess" if it had not been mapped to any other T^u considered before either. Since there are 1 + x ($x \geq 1$) R^{uu}_{phen}, x of them must be in "excess") or depends from an "excess" R^{uu}_{phen} (implicit or via PDB-cycle) then in the first case one maps that "excess" R^{uu}_{phen} to the $(1 + 1)^{st}$ T^u and in the second case one transfer the R^{uu}_{phen}-quality from the "excess" R^{uu}_{phen} to the depending new R_{phen}. In either case (13) becomes fulfilled. 2bb.) If it contains only R_{phen} which either are or depend only from R^{uu}_{phen} mapped to say, g, T^u considered before, then 2bba.) if one of these g T^u contains a second and therefore "excess" R^{uu}_{phen}, a transfer of mapping and/or R^{uu}_{phen} - quality can be made such that (13) becomes fulfilled. The same will be true if none of these g T^u contains an "excess" R^{uu}_{phen} but if by transfer of R^{uu}_{phen} - quality from an "excess" R^{uu}_{phen} contained in an other T^u considered before one of these g T^u can be made to contain one. If however, 2bbb.) this is not so, i.e. if the $(1 + 1)^{st}$ T^u and the g T^u together 1.) contain only g R^{uu}_{phen} and 2.) contain no R_{phen} which depend on R_{phen} contained in other T^u considered before, then these g + 1 T^u form a subset entirely uncoupled to the other T^u considered before which, for all g + 1 T to be T^u, would have to contain g + 1 R^{uu}_{phen} but which does not so that the $(1 + 1)^{st}$ T cannot be a T^u. So it follows that if the $(1 + 1)^{st}$ T is in fact a T^u one can always make it possible to map a R^{uu}_{phen} to it and since holds for all 1 and therefore, for all T^u of a set, (13) must always be true.

(22) can be seen by the following way:

For a n-component system and any given G^{n}_{mech}, the values of all k_{phen} are necessarily determined by and only by those of all k_{mech} (31). Of the k_{mech} the k_{XiJ} (see p.93) however will enter into this only by way of their $_{Xi}R^{u}_{mech}$, i.e. ratios of k_{mech} of equal origin X_i (32). This is so because we required quasistationarity of the X_i; i.e., the flow of matter to a particular X_i must equal the flow of matter from that X_i. Thus, since the later flow is tied to the former, the k_{XiJ} cannot determine its rate; they do determine, but only by way of their $_{Xi}R^{u}_{mech}$, its distribution among the different directions and this in turn will indirectly influence the rates of flow to X_i and thus the rate of flow from X. Since besides this the k_{XiJ} have no functions (32) follows.[5] Combining (31) and (32) we get: The $_{J}k_{mech}$ (= those k_{mech} whose origin is a reactant, J, not an X) and the $_{X}R^{u}_{mech}$ together determine the k_{phen}. If now the $_{J}k_{mech}$ are not given but only the $_{J}R^{u}_{mech}$, the information on the rates of flow from J is not given but only that on the distribution of flow among different directions. The same information loss results if the k_{phen} are not given but only the R^{u}_{phen}. From the last three sentences follows (22).

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[5] (32) means that vice versa one can never draw conclusions from the k_{phen} to the k_{XJ} but only to the $_{X}R_{mech}$. This means for chemistry: From the kinetic experiment one can find out the differences in energy and entropy between transition states around one X_i (since these are given by the $_{Xi}R_{mech}$), but never the energy and entropy (relative to the ones before) and the lifetime of that X_i (since these would be given by k_{XiJ}).

The reason for (27) can be seen in the following manner: According to (3a) to every edge in G^n_{mech} but for the first one one R^{uu}_{mech} can be mapped. The impossibility to cancel an edge therefore means the impossibility to counteract a change of the value of the R^{uu}_{mech} mapped to that edge (elimination of that edge means that it becomes 0 or ∞) by changing the values of the other R^{uu}_{mech} such that the values of the R^{uu}_{phen} remain unchanged. If this is true for all edges, i.e. for all R^{uu}_{mech}, then in analogy to the argument for a tree (see below) follows that the R^{uu}_{mech} are determined by the R^{uu}_{phen}.

(28) can be seen in the following manner: Since a change in the value of a R^{uu}_{mech} changes the distribution of flow of matter among different directions and since this distribution determines the R^{uu}_{phen} and since if there are no cycles in G^n_{mech} (which means that there is only one connection between any pair of reactants) that change cannot be compensated by changing the values of other R^{uu}_{mech} (except at the price of inducing more changes) it follows that a specific set of values of the R^{uu}_{phen} requires a specific value of that R^{uu}_{mech} and, since this holds for all R^{uu}_{mech} of the tree, it follows that it requires a specific set of values of all the R^{uu}_{mech}. This in other words means that the set of values of the R^{uu}_{mech} is determined by the set of values of the R^{uu}_{phen} and therefore, by the set of values of the R^{uuu}_{phen}.

(29) can be derived in the following manner: From (28) and (24c) we obtain for a tree: $u' + y = t - x + 1$ (33). Because of (18) u' can maximally be = t. The only G^n_{mech} to imply $u' = t$ is a star, i.e. a tree with $x = 1$. Inserting into (33) shows that for a star $y = 0$.

Upon transformation of the star into other trees by increasing x, every additional X will reduce u' by 1. (34). This with (33) gives (29).

To see (34) we note that for a given n there are trees with maximum x (viz.: $x = n - 2$) which differ in the type of branching. For all these trees $u' = (n - 2)(n - 3)/2$ as is found by systematic enumeration using (11). For the tree with minimum x (the star)

$u' = t = n(n - 3)/2.$

$\Delta u' = n(n - 3)/2 - (n - 2)(n - 3)/2 = n - 3.$

$\Delta x = 1 - (n - 2) = - (n - 3).$

Since with every additional X in a tree at least one ${}_1T^u$ must be lost, it follows from $\Delta u' = - \Delta x$ that with every additional X exactly one ${}_1T^u$ ist lost.

Acknowledgment

The promotion and encouragement of this work by Prof. O.E. Polansky are gratefully acknowledged.

Glossary

$\left(\frac{A}{B}\right)_C$ = ratio of products A and B when formed from C; it is equal to $\frac{k_{CA}}{k_{CB}}$; such a ratio is a R_{phen}; p.86

c = number of independent cycles (i.e. cycles which are not generated by cycles considered before) in G^n_{phen}; p. 87

c' = analogous to c in G^n_{mech} instead of G^n_{phen}; p.99

calculability, of a G^n_{mech}; definition p.99

contained (R_{phen} in T); definition p. 92

dependence, among four-cycles and T; definition p.91

e' = number of edges in G^n_{mech}; p. 95

G^n_{mech} = a mechanistic reaction graph for n reactants; p.93

G^n_{phen} = the phenomenological reaction graph for n reactants; p. 85

implicit dependence, among R_{phen} or R_{mech}; definition p. 86

k_{AB} = first order or pseudo first order reaction constant for the reaction A→B; p. 85

k_{mech} = a first order or pseudo first order reaction constant within a mechanistic reaction scheme, associated with an edge in G^n_{mech}; p. 93

k_{phen} = a phenomenological first order or pseudo first order reaction constant; p. 85

k^u_{phen} = a k_{phen} which is PDB-independent from k_{phen} considered before; p.86

n = number of reactants of a system

p = number of all k_{phen} in one n-reactant system; p.85

PDB = Principle of detailed balancing; p.85

q = number of all k^{u}_{phen} in one n-reactant system; p.86

R^{uu}_{mech} = a ratio of k_{mech} of equal origin; analogous to R^{uu}_{phen} in a mechanistic instead of the phenomenological reaction scheme; p.95

R_{phen} = see $\left(\frac{A}{B}\right)_C$

R^{u}_{phen} = a R_{phen} which is implicitly independent from R_{phen} considered before; p.86

R^{uu}_{phen} = a R^{u}_{phen} which is PDB-independent from R^{u}_{phen} considered before and from the R_{phen} which depend on them (implicitly or PDB); p.86

R^{uuu}_{phen} = a R^{uu}_{phen} which is not made dependent by G^{n}_{mech} from R^{uu}_{phen} considered before; p. 96

r = number of the R^{u}_{phen} of G^{n}_{phen}; p.86

s = number of the R^{uu}_{phen} of G^{n}_{phen}; p.86

s' = number of the R^{uu}_{mech} of G^{n}_{mech}; p.95

T = a ratio of the type $\left(\frac{A}{B}\right)_C$ / $\left(\frac{A}{B}\right)_D$; p.89

T^{u} = an independent T; definition p.91

$_{1}T$ = a T whose value is = 1; p.92

$_1T^u$ = a $_1T$ which is independent from $_1T$ considered before; p. ;for "dependence", see p.92

t = number of T^u in G^n_{phen}; p. 92

u = number of $_1T^u$ in a particular experimentally measured system; p. 93

u' = number of $_1T^u$ implied by G^n_{mech} ; p. 95

v = number of R^{uuu}_{phen} for a particular G^n_{mech}; p. 96

X = intermediate reaction stage which represents a branching point in G^n_{mech}; p. 93

x = number of X of a G^n_{mech}; p. 99

y = number of implications other than via $_1T^u$ by which G^n_{mech} makes R^{uu}_{phen} dependent from others; p. 96

Bibliography

1.) For methods to determine the k_{phen} from kinetic experiments, see
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