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AFFINITY AND REACTION RATE CLOSE TO EQUILIBRIUM

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I

The link between thermodynamic quantities and reaction rates has been discussed by numerous authors ever since the very beginning of modern physical chemistry (12, 18, 20). Yet in classical thermodynamics, limited essentially to the study of equilibrium states, research work has not led to very satisfactory results.

The theory of absolute rates of reaction, which we owe principally to H. Eyring and his school, demonstrates that the value of the kinetic constants of an elementary reaction is determined essentially by such thermodynamic quantities as energy and entropy of activation. On the other hand, these researches did not show whether or not any link exists between thermodynamic concepts and the value of the over-all reaction rate, a function of the kinetic constants and of the concentration.

To illustrate the point, let us consider the synthesis of hydriodic acid:

$$I_2 + H_2 \rightleftarrows 2HI$$

The reaction rate is

$$v = \overrightarrow{v} - \overleftarrow{v} = \overrightarrow{k}C_{I_2}C_{H_2} - \overleftarrow{k}C_{HI}^2 \tag{1}$$

where $\overrightarrow{v}$ and $\overleftarrow{v}$ represent the rates of the two opposite reactions and $\overrightarrow{k}$ and $\overleftarrow{k}$ the corresponding kinetic constants.

The study of the relationship between the over-all rate close to equilibrium and the thermodynamic concepts is the object of the present work.

This problem can be readily studied by employing the methods of the chemical thermodynamics of irreversible phenomena, which we owe principally to Th. De Donder (2, 3, 4) and his school (15, 16, 17) and also to Eckart (5), Onsager (14), Meixner (13), etc. Let us recall briefly some results which we shall need here.

The presence of irreversible phenomena is characterized thermodynamically by a definite positive production of entropy. We can say that irreversible phenomena (diffusion, thermal or electric conduction, chemical reactions) create entropy but cannot destroy it. In systems at uniform temperature, this production of entropy is none other than the non-compensated heat of Clausius divided by the absolute temperature.

Let us limit ourselves to uniform systems (without diffusion) in mechanical and thermal equilibrium. The only irreversible phenomenon which we shall then have to consider is the chemical reaction. It is proved that the production of entropy per unit of time, due to a chemical reaction, is

$$\frac{Av}{T} > 0 \tag{2}$$

where v is the rate of the reaction, T the absolute temperature, and A the chemical affinity. Th. De Donder has shown that this affinity can be easily calculated; for example, from the chemical potentials μ_γ we have

$$A = -\sum_{\gamma} \nu_\gamma \mu_\gamma \tag{3}$$

where ν_γ is the stoichiometric coefficient of the constituent γ in the reaction.

Formula 2 gives us directly the fundamental inequality of De Donder:

$$Av > 0 \tag{4}$$

Affinity and reaction rate have therefore the same sign. At thermodynamic equilibrium we have simultaneously:

$$A = 0, \qquad v = 0 \tag{5}$$

Let us note that equations 4 and 3 are quite independent of the particular conditions in which the chemical reaction takes place (e.g., V and T constant or P and T constant).

These relations express an intrinsic connection between reaction rates and thermodynamic concepts. Let us examine more closely their kinetic consequences.

II

A reaction rate is a function of different macroscopic variables such as concentration, temperature, and mass of catalyst. Let us call $x_1, x_2 \cdots x_{\lambda+1}$ these different variables. Thus:

$$v = v(x_1, x_2, \cdots x_{\lambda+1}) \tag{6}$$

The affinity A of the reaction is equally a function of some at least of these variables.

$$A = A(x_1, x_2 \cdots x_{\lambda+1}) \tag{7}$$

Let us eliminate one of the variables, $x_{\lambda+1}$ for example, between equations 6 and 7, from which we obtain:

$$v = f(x_1 \cdots x_\lambda, A) \tag{8}$$

By virtue of equation 3 the function thus obtained cancels itself out at the same time as the affinity A. Thus

$$f(x_1, x_2 \cdots x_\lambda; 0) = 0 \tag{9}$$

This holds whatever the values of $x_1 \cdots x_\lambda$ may be.

Let us develop f in a power series of the variable A. By virtue of equation 9 we obtain a linear law between v and A close to equilibrium.

$$v = \left(\frac{\delta f}{\delta A}\right)_{x_1 \cdots x_\lambda} \cdot A \tag{10}$$

The angular coefficient

$$a \equiv \left(\frac{\delta f}{\delta A}\right)_{x_1 \cdots x_\lambda} \tag{11}$$

is generally a function of λ variables. If, in the course of different experiments, these variables maintain constant values, this angular coefficient will also retain a constant value. Let us also observe that on account of the inequality 4 and of equation 10 the angular coefficient (equation 11) is positive.

Let us first show by a simple example that the linear law (equation 10) is perfectly in accord with the form which the usual laws of kinetics assume close to equilibrium. Let us return again to example 1. By using relation 3 between affinity and the chemical potentials, equation 1 can easily be expressed in the form:

$$v = \overrightarrow{k} C_{I_2} C_{H_2} (1 - e^{-(A/RT)}) \tag{12}$$

In the case of a perfect gas the chemical potentials are of the form

$$\mu_\gamma = \mu_\gamma^0(T) + RT \log C_\gamma$$

where $\mu_\gamma^0(T)$ depends only on the temperature. By virtue of equation 3 the affinity of the reaction (1) takes in that case the form:

$$A = RT \log \frac{K(T)}{C_{I_2}^{-1} C_{H_2}^{-1} C_{HI}^2}$$

where $K(T) = \dfrac{\overrightarrow{k}}{\overleftarrow{k}}$ is the constant of Guldberg and Waage. In using this value of affinity, formula 1 immediately takes the form of expression 12.

Close to equilibrium we have:

$$\left|\frac{A}{RT}\right| \ll 1 \tag{13}$$

from which we have

$$v = \vec{k}\, C_{I_2} C_{H_2} \frac{A}{RT} \tag{14}$$

We thus find again the linear law (equation 10).

We observe besides that the angular coefficient (equation 11) has a simple physical significance.

The linear relation (equation 10) has a double aspect. On the one hand, owing to its thermodynamic character, it has an extreme generality. It is independent of all hypotheses as to the mechanism of the reaction. Furthermore, relations of this type are found in all irreversible phenomena. Thus in the case of a system at non-uniform temperature a "thermal affinity" can be introduced, linked to the gradient of temperature. The linear relation between affinity and reaction rate is then reduced to Fourier's classical law. The laws of diffusion, viscosity, or thermodiffusion are obtained in an analogous manner.

On the other hand, formula 10 holds only close to equilibrium. As soon as we move away from equilibrium the relation between affinity and rate becomes more complex.

III

The relations which we have obtained are easily extended to the case where the system under consideration is the seat of many simultaneous chemical reactions. The fundamental inequality of De Donder (3), expressing the positive production of entropy, becomes

$$\sum_{\rho} A_\rho v_\rho > 0 \tag{15}$$

where v_ρ is the rate of the ρ^{th} reaction and A_ρ its affinity. At thermodynamic equilibrium we have simultaneously

$$A_\rho = 0; \quad v_\rho = 0 \quad (\rho = 1 \cdots r) \tag{16}$$

while close to equilibrium we shall have the linear and homogeneous laws between affinities and rates:

$$v_\rho = \sum_{\lambda} a_{\rho\lambda} A_\lambda \tag{17}$$

It can easily be shown that the usual kinetic laws lead, close to equilibrium, to formula 17.

In all the simple cases we have moreover $a_{\rho\lambda} = 0$ for $\rho \neq \lambda$ and relations 17 are reduced to:

$$v_\rho = a_{\rho\rho} A_\rho \tag{18}$$

each rate becoming proportional to its affinity.

These formulae lead us to several interesting conclusions. To illustrate the point let us consider a series of consecutive reactions. For example:

$$\begin{array}{c} \mathrm{M} \rightleftarrows \mathrm{N} \\ \vdots \\ \mathrm{P} \rightleftarrows \mathrm{F} \end{array} \tag{19}$$

The rate at which the final product F appears is equal to the rate of the r^{th} reaction and will be proportional, by virtue of equation 18, to the affinity A_r. When the intermediate product P is unstable, its concentration is difficult to measure and the affinity A_ρ is not generally accessible to calculation. Nevertheless, when a quasi-steady state is established, where all the rates of the consecutive reactions become equal, we have:

$$v = v_1 = v_2 = \cdots = v_r \tag{20}$$

and by virtue of equation 18

$$a_{11}A_1 = a_{22}A_2 = \cdots = a_{rr}A_r \tag{21}$$

from which, representing the total affinity of the reaction by $A = \sum_\rho A_\rho$,

$$\frac{A_1}{\dfrac{1}{a_{11}}} = \frac{A_2}{\dfrac{1}{a_{22}}} = \cdots = \frac{A_r}{\dfrac{1}{a_{rr}}} = \frac{A}{\sum\limits_\rho \dfrac{1}{a_{\rho\rho}}} \tag{22}$$

The rate at which the final product appears becomes thus

$$v = v_r = \frac{A}{\sum\limits_\rho \dfrac{1}{a_{\rho\rho}}} \tag{23}$$

Thus the rate becomes proportional to the total affinity A. In particular, v is cancelled out for $A = 0$, while outside of the quasi-steady system v is cancelled out in conformity with equation 18 for $A_r = 0$ but can be different from zero for $A = 0$.

We can call $1/a_{\rho\rho}$ the relative "reaction resistance" to the partial reaction ρ and $\sum_\rho 1/a_{\rho\rho}$ the "total reaction resistance."

When one stage is particularly slow—for example, that which corresponds to the j^{th} reaction—we have

$$a_{jj} \ll a_{\rho\rho} \text{ for } \rho \neq j$$

and formula 23 is reduced to

$$v_r = a_{jj}A \tag{24}$$

In other terms, the rate at which the final product appears is governed by the total affinity and by the reactional resistance of the rate-determining j^{th} step only.

A formula, analogous to equation 23, valid for the coöperation between dissolution and diffusion, was established by Fischbeck (16).

IV

In the present work we have verified the validity of linear relations between affinities and reaction rates. We have chosen the antagonistic reactions of hydrogenation of benzene and of dehydrogenation of cyclohexane, because these complex reactions have been the object of detailed kinetic studies in our laboratory (8–11). On the one hand, the experiments consist in the measurement of resulting rates of antagonistic reactions under carefully determined conditions of temperature and partial pressures, and on the other hand in the measurements of constants of equilibrium at different temperatures. A knowledge of the constants of Guldberg and Waage are in fact necessary in the calculations of the affinities of gaseous mixtures.

The apparatus, the preparation of the catalysts, and the experimental technique have been described in previous papers (8). Let us simply recall that the experiments were carried out by the flow method.

The principle of the determination of instantaneous rates of reaction by the dynamic method has been established by Herbo (8). If a gaseous mixture of hydrogen and benzene of invariable composition but of increasing flow is directed towards the chamber of reaction, the yield per hour (that is, the quantity of benzene transformed per unit of time) tends asymptotically towards a maximum. On the contrary, the rate of transformation (that is, the ratio of benzene transformed to the quantity transformable when the reaction is complete) tends asymptotically towards zero (see also on this subject Damköhler (1)). Let D_e and D_s denote, respectively, the flow of benzene at the entrance and the exit of the reaction chamber, and θ and v the rate of transformation and the yield per hour. By definition we have:

$$\theta = \frac{D_e - D_s}{D_e}$$

$$v = D_e - D_s, \qquad \text{hence} \qquad v = \theta D_e$$

For sufficiently large flows the rate of transformation is inversely proportional to the flow D_e. Under these conditions, the yield per hour is maximum and independent of the flow. Let us show that this yield can be identified with the instantaneous rate of the reaction. Let us divide the reaction chamber in our minds into elementary volumes. The yield per unit of time in each of these volumes increases as the steady concentrations of the reactants come closer to the initial concentrations. If the flow of the gaseous mixture is sufficiently large, the concentrations of the reactants in the last element of volume are indefinitely close to the concentrations in the first element. Under these conditions, the sum of the elementary yields is maximum and cannot increase further with the flow of the gaseous mixture. It is really a question of initial rate of reaction, since the partial pressures of the gaseous constituents are infinitely close to the initial partial pressures in the entirety of the reaction chamber. If a mixture of hydrogen, benzene, and cyclohexane is directed towards the reaction chamber, the maximum yield is a measure of the initial rate resulting from the two antagonistic reactions (v'). Let us express this resulting rate in grams of benzene transformed per unit of time and let us consider it as positive if there is formation of benzene and as negative in the opposite case. Thus:

$$v' = D_s - D_e$$

The affinity A of the gaseous mixture under the same conditions of temperature and partial pressures is given by the formula:

$$A = RT(\log K + \log P_c - \log P_b - 3 \log P_h)$$

where R is the constant of perfect gases in calories mole^{-1} degree^{-1}, T is the temperature in degrees Kelvin, P_c, P_b, and P_h are the partial pressures in atmospheres of the three constituents of the gaseous mixture, and K is the equilibrium constant of Guldberg and Waage:

$$K = \frac{(P_b)_e(P_h)_e^3}{(P_c)_e} \tag{25}$$

The measurements of K at different temperatures have been made in two different ways. In the first series of experiments, we have directed gaseous mixtures of hydrogen, benzene, and cyclohexane towards the reaction chamber. From one experiment to another we have modified the temperature of the catalyst and we have measured in each case the corresponding maximum yield. If the antagonistic reactions are indicated by a formation of benzene ($D_s > D_e$), the yield per hour is positive. If, on the contrary, the reaction of hydrogenation outweighs the reaction of dehydrogenation, the hourly yield is negative ($D_s < D_e$). The temperature at which the gaseous mixture passes on to the catalyst without being transformed is determined by graphic interpolation ($D_s = D_e$). It is the temperature at which the initial mixture is in equilibrium. K is calculated by means of equation 25, by taking:

$$P_h = (P_h)_e, \quad P_b = (P_b)_e, \quad \text{and } P_c = (P_c)_e$$

in another series of experiments we have directed towards the catalyst, which is kept at a constant temperature, gaseous mixtures of well-known composition. From one experiment to another we have systematically modified the proportion of the three constituents, and in each case we have measured the corresponding maximum yield. This time, we obtain by graphic interpolation the composition of the gaseous mixture in equilibrium at the temperature of the catalyst. These two series of determinations have given values for K in agreement with the formula of Schultze (19) within the range of experimental errors:

$$\log K = \frac{51{,}500}{4.573\, T} - 20.69$$

Tables 1 and 2 and figures 1–6 reproduce some of the results obtained.

These experimental results show that the linear law between reaction rate and affinity is well satisfied in a wide region on both sides of the state of equilibrium of the reaction:

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$$

TABLE 1

Affinity and reaction rate in the system hydrogen–benzene–cyclohexane

Catalyst: 50% Ni, 25% ZnO, 23% Cr_2O_3 (mole per cent). Weight of catalyst: 200 mg.

PARTIAL PRESSURES			RATIO A/R	v'	TEMPERATURES
P_b	P_c	P_h			
atm.	*atm.*	*atm.*		*grams per hour*	°*K.*
0.0242	0.104	0.899	−720	−29	488
	(see figure 1)		−531	−21.5	498
			−274	−9	509
			+16	+1	523
			+231	+7	533
			+403	+16	546
0.0172	0.252	0.771	−188	−9	501
	(see figure 2)		+73	+1	513
			+293	+10.5	523.5
			+589	+20	535
0.0487	0.0784	0.912	−812	−32	497
	(see figure 3)		−217	−13	522
			−60	−4.5	533
			+172	+4.5	544
			+403	+14.5	555
			−139	−7	529
			−583	−24	510
			−812	−33.5	497
0.0977	0.0262	0.925	−1150	−36	500
	(see figure 4)		−686	−21	524
			−271	−11.5	545
			−85	−3	554
			+84	+1	561
			+323	+8	571
			+526	+13	582

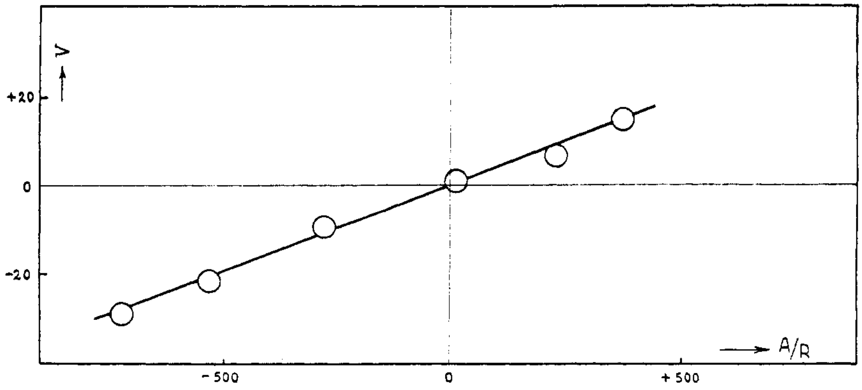

FIG. 1. Rate of formation of benzene in grams per hour plotted against the ratio of affinity to molar gas constant. First set of data of table 1.

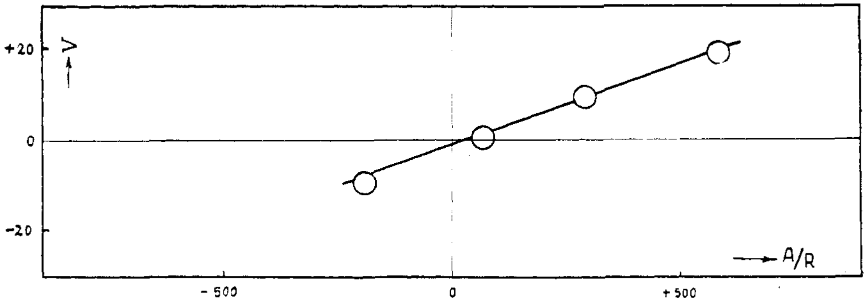

FIG. 2. Rate of formation of benzene in grams per hour plotted against the ratio of affinity to molar gas constant. Second set of data of table 1.

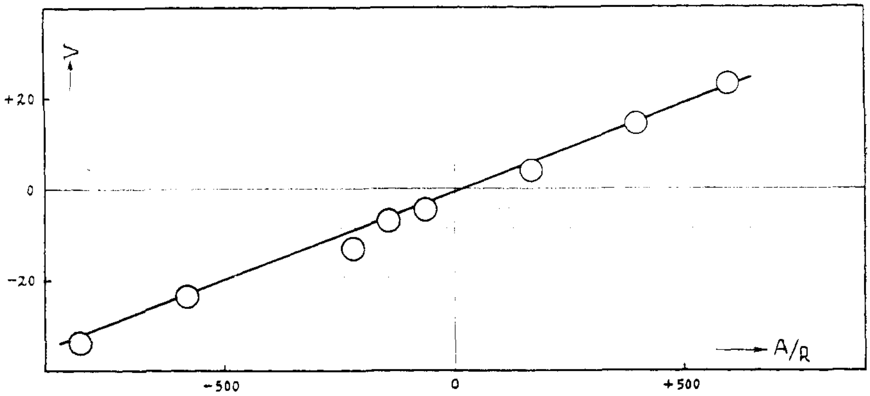

FIG. 3. Rate of formation of benzene in grams per hour plotted against the ratio of affinity to molar gas constant. Third set of data of table 1.

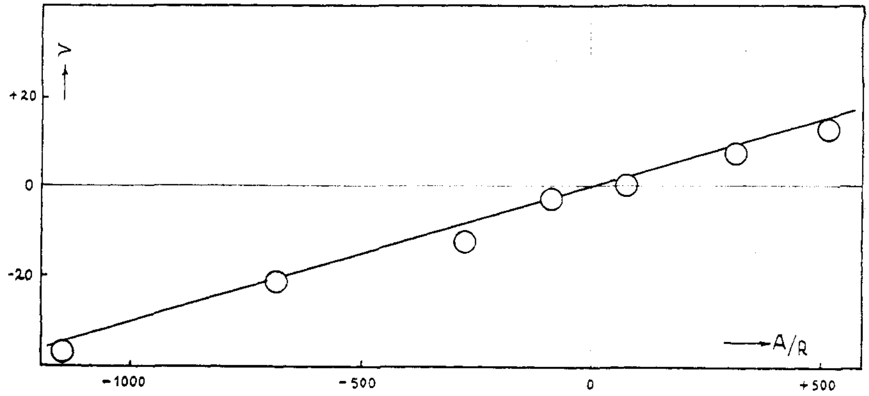

FIG. 4. Rate of formation of benzene in grams per hour plotted against the ratio of affinity to molar gas constant. Fourth set of data of table 1.

Thus in the case of mixtures having a constant composition but studied at different temperatures, the linear law has been verified in an interval of temperature of about 100°C.

TABLE 2

Affinity and reaction rate in the system hydrogen–benzene–cyclohexane

Catalyst: 50% Ni, 10% ZnO, 40% Cr_2O_3 (mole per cent)

WEIGHT OF CATALYST	PARTIAL PRESSURES			RATIO A/R	v'	TEMPERATURE
	P_b	P_c	P_h			
mg.	*atm.*	*atm.*	*atm.*		*grams per hour*	°*K.*
175	0.179	0.073	0.792	−197	−24	548
(see figure 5)	0.204	0.048	0.790	−323	−31	
	0.051	0.195	0.799	+328	+32	
	0.107	0.145	0.796	+86	+9	
	0.154	0.097	0.792	−92	−15	
	0.128	0.121	0.797	0	−1	
	0.077	0.017	0.786	+227	+29	
	0.179	0.073	0.781	−154	−21	
	0.128	0.121	0.782	+1	+1	
50	0.294	0.024	0.714	$-690/R$	−8	563
(see figure 6)	0.225	0.042	0.765	0	−1	
	0.100	0.075	0.859	+996	+11	
	0.146	0.063	0.825	+690	+7	

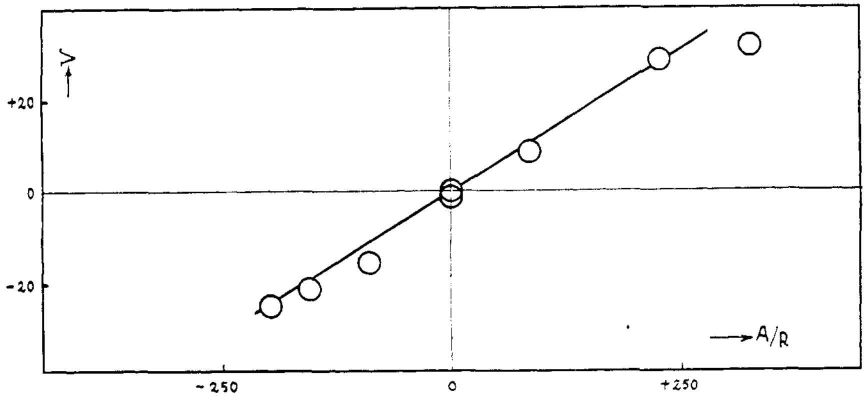

FIG. 5. Rate of formation of benzene in grams per hour plotted against the ratio of affinity to molar gas constant. First set of data of table 2.

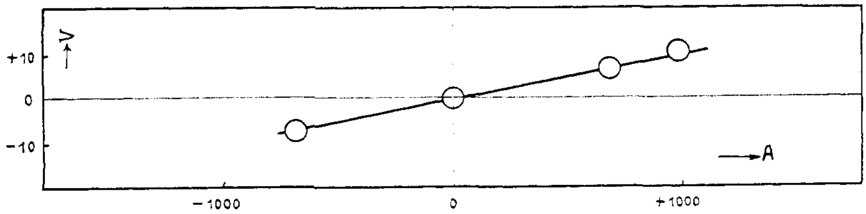

FIG. 6. Rate of formation of benzene in grams per hour plotted against the affinity. Second set of data of table 2.

Let us note that in experiments 5 and 6 the predictions of the theory are exceeded, for the theory requires a linear law if one only of the variables is modified (*cf.* Section II). On the contrary, in the series of experiments 5 and 6 the values of the three partial pressures P_c, P_b, and P_h are modified simultaneously. The angular coefficient a (equation 11) should vary. In fact a remains constant in a wide interval, which shows that the influence exercised on a by the composition of the gaseous mixture must be very slight.

Let us again observe that, the reaction rate being proportional to the over-all affinity of the succession of consecutive reactions which lead from benzene to cyclohexane, we can, by virtue of the developments of Section III, see in this an argument in favor of the fact that a quasi-steady regime is obtained on the surface of the catalyst.

SUMMARY

The thermodynamics of irreversible phenomena, based mainly on the concept of entropy production, leads to linear and homogeneous relations between affinities and reaction rates close to equilibrium. These laws have been verified experimentally in the case of the catalytic reaction of the hydrogenation of benzene and the inverse reaction of the dehydrogenation of cyclohexane. The method used for measuring rates is the dynamic method of high flow rates. The domain of validity of these laws is discussed. In a quasi-steady state, particularly simple relations are established.

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