TABLE VII

CORRECTIONS TO BE APPLIED TO CONDUCTANCE DATA BASED ON KOHLRAUSCH STANDARD POTASSIUM CHLORIDE SOLUTIONS

	0°	18°	20°	25°
1 *N* KCl 71.3828 g. KCl per 1000 g. of solution in vacuum				
Kohlrausch	0.06541	0.09822	0.10207	0.11180
Parker's values	.065312	.098116		.111687
Parker's corrections, %	− .150	− .108		− .101
Our new values	.065430	.098201	.102024	.111733
Recommended corrections, %	+ .031	− .019	− .045	− .060
0.1 *N* KCl 7.43344 g. KCl per 100 g. solution in vacuum				
Kohlrausch	0.00715	0.01119	0.01167	0.01288
Parker's values	.0071416	.0111846		.0128765
Parker's corrections, %	− .118	− .048		− .027
Our new values	.0071543	.0111919	.0116676	.0128862
Recommended corrections, %	+ .060	+ .017	− .021	+ .048
0.01 *N* KCl 0.746558 g. KCl per 1000 g. solution in vacuum				
Kohlrausch	0.000776	0.001225	0.001278	0.001413
Parker's values	.00077422	.00122238		.00141037
Parker's corrections, %	− .229	− .214		− .186
Our new values	.00077512	.00122269	.00127572	.00141145
Recommended corrections, %	− .114	− .189	− .179	− .110

Parker's standards instead of the Kohlrausch standards originally used by most experimenters.

Summary

1. The absolute specific conductances of the 1, 0.1 and 0.01 *N* potassium chloride solutions recommended by Kohlrausch as a standard of reference for conductivity measurements have been redetermined.

2. The results indicate that the corrections used by the "International Critical Tables" in the recalculation of the conductance data are unreliable.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of Activated Sorption of Hydrogen on Chromic Oxide Gel[1]

BY LOYAL CLARKE,[2] L. S. KASSEL[3] AND H. H. STORCH[4]

Introduction

Burwell and Taylor[5] have recently presented more than usually complete data on the kinetics of activated sorption of hydrogen on a chromium oxide catalyst as a function of pressure and temperature. The present paper derives from their data an empirical relationship which is satisfactory, except for small and for very large sorption. The form of this relation suggests a model of the sorption process, which permits derivation of the equation for moderate sorptions, and accounts at least qualitatively for its failure at extreme conditions.

When the amount of hydrogen sorbed computed by Burwell and Taylor is plotted against time and a smooth curve drawn through the points, it was found that extrapolation to the starting time would, taken naïvely, indicate an appreciable amount of sorption coincident with the beginning of the experiment. The results of these extrapolations are given in Table I. It will be seen that for all the experiments at 1 atmosphere this initial amount is about 1.3 cc., at one-half atmosphere about 0.8, and at a quarter atmos-

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(5) R. L. Burwell, Jr., and H. S. Taylor, THIS JOURNAL, 58, 697–705 (1936).

TABLE I

EXTRAPOLATION OF SORPTION DATA TO STARTING TIME

Temp., °K.	383.5	405	427	457	491	457
Catalyst	9	9	9	9	9	10
Extrapolation in cc. when pressure is:						
1 atmosphere	1.34	1.42	1.26	1.30	1.20	1.21
$^1/_2$ atmosphere	0.76	0.86	0.80	0.80	0.80	0.96
$^1/_4$ atmosphere	.57	.50	.43	.50	.50	.43
$^1/_8$ atmosphere						.15

phere 0.5, or approximately $0.2 + 1.1\,p$. It is quite possible that the dead-space determination using helium is not the correct dead space available for hydrogen,[6] but regardless of cause it is believed that a large fraction of these initial amounts represents a phenomenon other than the slow sorption process.[7] Accordingly the amounts sorbed, as given by Burwell and Taylor, have been corrected by subtraction of the extrapolations given in Table I. The corrected figures appear to approximate the true amount of activated sorption. This is indicated by the improved correlations obtained by means of the revised data.

Burwell and Taylor observed that the data of the separate experiments would approximate a common curve when the amount of sorption, S, is plotted against bt, where b is a constant whose relative value is characteristic of the pressure and the temperature. This relation is, as Burwell and Taylor themselves state, only approximate, but it is improved somewhat by the use of our revised values instead of the uncorrected data. The representation of b by the equation $b = p^nAe^{-Q/RT}$ suggested by Burwell and Taylor is also improved but still inadequate, since the best values of n computed at 383.5, 405, 427, 457, and 491°K. were, respectively: 1.00, 1.00, 0.84, 0.74, and 0.60. Values of Q in the temperature range of 405 to 491°K. as graphically computed from mean values of $p^{0.8}t$ at sorptions of 1, 2, 3, 4, 5 and 6 cc. were, respectively: 15.3, 18.3, 19.0, 19.2, 19.7 and 21.0 kcal. Little impart may be attached to the 1 cc. value and the trend in the other values is comparable with the accuracy of computation and would not be serious were it not that the fluctuation of n impairs the utility of the relation and obscures the interpretation of Q as an activation energy.

Kinetic Model

The existence of a pressure effect definitely less than first order seems to force the assumption that the initial sorption process is followed by some more or less slow rearrangement. We propose to investigate the consequences of this assumption in a relatively simple form. It will be supposed that the sorbent contains n primary adsorption centers and N secondary centers, only the former of which are capable of capturing gas molecules. The secondary centers can take molecules from, and give molecules to, the primary centers but have no kinetic relations with the gas. The fraction of primary centers covered is Θ, that of secondary centers is α, and the gas pressure is p. The rates of the various allowed transfers, in molecules per secondary are then taken to be as

gas ⟶ primary centers	$npk_1\,(1 - \Theta)$
primary ⟶ secondary centers	$nNk_2\Theta\,(1 - \alpha)/(1 + R\alpha)$
secondary ⟶ primary centers	$nNk_3\alpha\,(1 - \Theta)/(1 + R\alpha)$
primary centers ⟶ gas	$nk_4\Theta$

The significance of the factor $1 + R\alpha$ will be discussed later in the paper. The controlling differential equations are then

$$\mathrm{d}N\alpha/\mathrm{d}t = nN[k_2\Theta\,(1 - \alpha) - k_3\alpha\,(1 - \Theta)]/(1 + R\alpha)$$
$$\mathrm{d}(n\Theta + N\alpha)/\mathrm{d}t = n[pk_1\,(1 - \Theta) - k_4\Theta]$$

If n and N are of the same order of magnitude we proceed as follows:

(1) Define a new variable β, proportional to the total adsorption, by the relation

$$n\Theta + N\alpha = n\beta$$

and use this relation to eliminate α from the differential equations.

(2) Introduce for Θ the power series expansion

$$\Theta = \beta + u_2\beta^2 + u_3\beta^3 + \ldots$$

obtaining two differential equations of the form

$$\mathrm{d}\beta/\mathrm{d}t = f\,(\beta)$$

(3) Expand the two right-hand members and determine the parameters u_i by equating coefficients of like powers of β.

(4) Solve the resulting single differential equation for t as a power series in β.

The result is

$$t = \beta/pk_1 + (1/pk_1 + k_4/p^2k_1^2)(\beta^2/2) + \ldots$$

The coefficients of β and β^2 do not have the form of pressure dependence necessary to give an

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[6] *Cf.* experiments reported by Benton at Pittsburgh meeting of American Chemical Society, September 7–12, 1936.

[7] Burwell and Taylor also suggested that a certain amount of the hydrogen loss was due to causes other than the one of interest and treated their data both with and without appropriate corrections therefore. We found difficulty in understanding the method of deduction of these values and have chosen the above method because it is direct, independently reproducible, and reasonably free from predisposition toward any particular relationship connecting the data at various pressures and temperatures.

apparent order less than unity and this model is thus unsatisfactory. The secondary centers, in fact, do not enter into these coefficients at all; k_2 first appears in the coefficients of β^3, and k_3 in that of β^4.

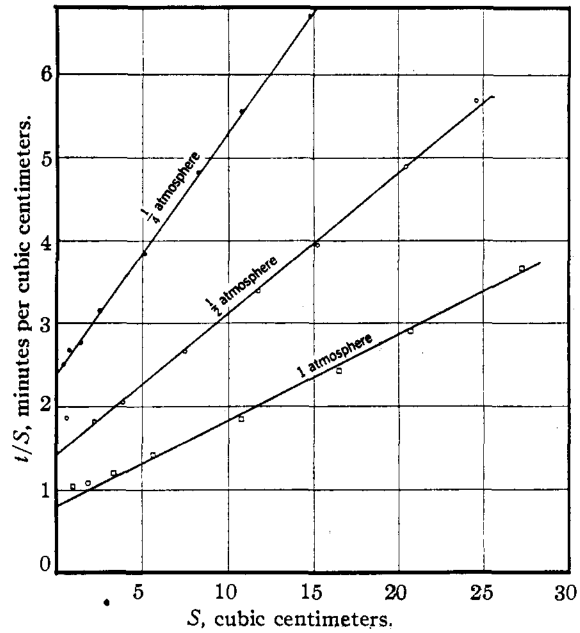

Fig. 1.—Sorption data at 457°K.

If n is very small compared to N, which is certainly a plausible condition, the foregoing analysis remains perfectly correct, but is no longer useful. Moderate values for β, such that terms beyond β^2 may be discarded, correspond to extremely small values of the total absorption, quite outside the range of measurement. A more appropriate solution for this case is obtained by a method similar to that used for chain reactions. Since, beyond the very earliest stages of the reaction, $n\Theta \ll N\alpha$, it follows that $\mathrm{d}n\Theta/\mathrm{d}t \ll \mathrm{d}N\alpha/\mathrm{d}t$. We may therefore use

$$\mathrm{d}n\Theta/\mathrm{d}t = 0$$

to determine a steady state value of Θ as a function of α. This functional relation is used to eliminate Θ, giving a differential equation of the form $\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)$ which has as a solution the power series expansion

$$\begin{aligned} nt = {} & [1/k_2 + (N/k_1 + k_4/k_1k_2)(1/p)]\alpha \\ & + (1/2)\{((R+1)/k_2 + [(R+1)k_4/k_1k_2 + Nk_3/k_1k_2 \\ & + k_3k_4/k_1k_2^2)](1/p) \\ & + (Nk_3k_4/k_1^2k_2 + k_3k_4^2/k_1^2k_2^2)(1/p^2)\}\alpha^2 + \ldots \end{aligned}$$

When $k_4 \ll k_1p$, which is true at pressures where the equilibrium adsorption is large, the terms in $(1/p^2)$ make a negligible contribution to the coefficient of α^2.

Using the assumptions $k_4 \ll k_2N$ and $k_4 \ll k_1p$, both of which are probably justified, we obtain

$$nt = (1/k_2 + N/k_1p)\alpha + 1/2[(R+1)/k_2 + Nk_3/k_1k_2p]\alpha^2$$

Application to Data of Burwell and Taylor

$N\alpha$ is obviously the amount of sorption and is conveniently designated by a single letter S. We make the further substitutions

$$\frac{1}{nk_1} = B_1,\ \frac{1}{nKk_2} = B_2,\ \frac{k_3}{2nNk_1k_2} = C_1,\ \frac{R+1}{2nN^2k_2} = C_2$$

and obtain

$$pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$$

The experiments of Burwell and Taylor were performed at constant pressures so that the coefficients of S and S^2 should be constant for any single experiment.

A plot of t/S against S should therefore be a straight line. Burwell and Taylor's data (corrected as described) for catalyst 9 at 457°K. are so plotted in Fig. 1. The relation is adequate for values of adsorption between 2.5 and 25 cc. The B_2 and C_2 terms are relatively unimportant at 383.5 and 405°K., so that the data for different pressures fall on a comparatively straight line when pt/S is plotted against S as in Fig. 2.

The best values of these constants are given in Table II under the heading "experimental."

Returning to the significance of these constants in the kinetic derivation

$$\begin{aligned} k_1 &= 1/nB_1 \\ k_2 &= 1/nNB_2 \\ k_3 &= 2C_1/nB_1B_2 \\ R + 1 &= 2NC_2/B_2 \end{aligned}$$

TABLE II

BEST VALUES OF CONSTANTS IN THE EQUATION $pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$. UNITS p IN ATM., t IN MINUTES, S IN CC.

	B_1		B_2		C_1		C_2	
T, °K.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.
383.5	1.2	23.5	0	11.5	11.6	12.4	0	0.92
405	2.9	6.67	0	3.80	3.14	2.31	0	.30
427	2.05	2.09	1.275	1.38	0.44	0.47	0.11	.11
457	0.49	0.47	0.43	0.41	.064	.063	.033	.033
491	.112	.122	.125	.123	.0101	.0103	.0095	.0098

The "theoretical" values of the constants given in Table II are computed from the equations

$$\log \frac{B_1}{\sqrt{T}} = \frac{4110}{T} - 10.63$$

$$\log B_2 = \frac{3450}{T} - 7.94$$

$$\log \frac{C_1}{B_1 B_2} = -\frac{2060}{T} + 4.03$$

$$C_2/B_2 = 0.08$$

The values for the lower temperatures are in disagreement with these equations; however, the total amount of sorption at these temperatures is small and, in fact, of the order for which the relation fails at higher temperatures. This failure is consistent with the theoretical analysis made above. Furthermore, this is not unexpected since the subtractive corrections as determined by the experimental intercepts are of the same order of magnitude as the total sorption at the lower temperatures.[8] The relation $pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$ is therefore of a semi-empirical nature when used in experiments involving very small sorptions.

The theoretical value of the ratio C_2/B_2 is $(R + 1)/2N$. The experimental value is approximately 0.08, and hence $\alpha = 0.16\ S/(R + 1)$. If $R = 0$, $\alpha = 1$ would correspond to $S = 6.25$ cc., whereas actually the saturation absorption is probably 100 cc. or more. The value of R needed to agree with these data is therefore at least 15. This necessary correction factor, $(1 + R\alpha)^{-1}$, may be interpreted as representing a reduced rate of transfer between primary centers and non-adjacent secondary centers; its form, however, is determined by mathematical convenience rather than physical considerations.

The experimental results for the highest three temperatures then give for k_1 an activation energy of 18.75 kcal., for k_2, 15.75 kcal. and for k_3, 9.4 kcal. The relative activation energies for k_2 and k_3 indicate a heat of adsorption for the primary centers 6.3 kcal. greater than for the secondary centers. This difference is consistent with the greater activity of the primary centers in adsorbing gas molecules. If the rate of adsorption on the primary centers is equal to the rate of collision of gas molecules $Xe^{-19{,}000/RT}$, the area of these centers must be 1600 sq. cm. They would then have an adsorptive capacity of the order of 0.5 cc. This value is sufficiently small to justify the assumption $n \ll N$. It is, at the same time, large enough to make this assumption slightly erroneous, and thus perhaps to account for the observed systematic distortions in the experimental curves for adsorptions less than 2.5 cc.

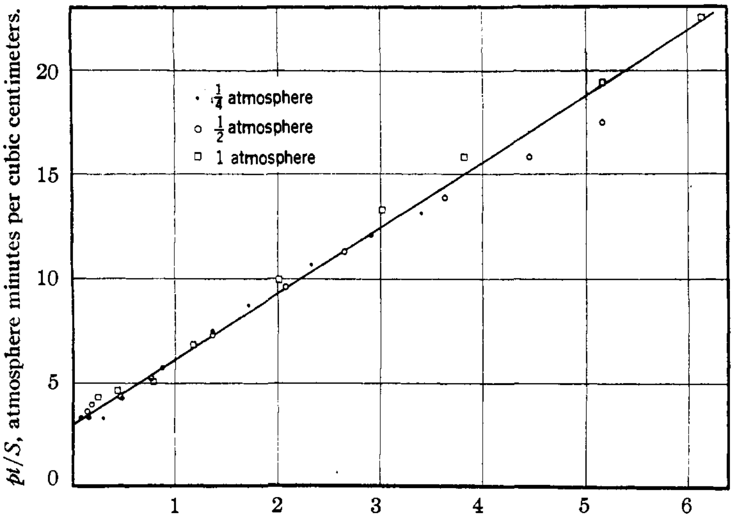

Fig. 2.—Sorption data at 405°K.

Discussion

The failure of results at the lowest temperatures to agree with extrapolated constants is quite possibly associated with the great importance of the amount of primary adsorption for the

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[8] The method used in adjusting the data implicitly assumes that the activated sorption of hydrogen on secondary centers is the only process resulting in an appreciable withdrawal of hydrogen after the first few minutes. Burwell and Taylor have suggested that some of the sorption occurring after several minutes also represents phenomena other than that of interest and should be included in the subtractive corrections. It has been found possible to secure excellent agreement between equations obtained by the use of the theoretical constants given in Table II and the data for the latter portion of the runs at 383.5°K. (after forty minutes) and 405°K. (after twenty minutes) by subtraction from the original data of the following constants:

p, atm.	383.5°K.	405°K.
1	2.25 cc.	2.08 cc.
0.5		1.38
.25	1.30	0.85

The difference between these values and our previous corrections may represent either primary sorption or an entirely unrelated process, or both. This suggests the adoption of a more refined method of determining the corrections. This could be done by fitting the original data to equations of form: $t = a + bS + cS^2$ and computing the subtractive corrections and the other constants therefrom. The foregoing analysis would be used only for rejection of points outside of the expected range of validity. Such a revision has not been undertaken however, because the high temperature experiments would still have to carry the burden of the proof and their interpretation would not be materially altered.

small sorptions to which data at these temperatures are limited.[8] It does not appear possible to decide definitely whether this type of analysis is applicable to the lower temperatures without extensions of the data to larger sorptions. For the higher-temperature region, however, there seems little doubt that the model yields a satisfactory interpretation of the experimental data. It does not follow that the underlying assumptions are entirely correct. As has already been suggested, the correction factor $(1 + R\alpha)^{-1}$ is introduced in an arbitrary way.

A precise treatment of the diffusion factor would necessitate a consideration of the geometry of the model. Such an analysis might conceivably result in a decision as to whether the phenomenon of slow sorption on chromic oxide gel corresponds more closely to a surface diffusion from active centers,[9] to surface adsorption followed by diffusion to the interior,[10] or to diffusion into Smekal cracks.[11] The assumption that there is no direct sorption on the secondary centers can represent at best merely an approximation to the case where the amount of such sorption is small. The sorptive regions of a real catalyst may not be amenable to a classification as simple as that which we have used, and although the introduction of more types of centers would probably lead to equations of the same form as we have found, the experimental constants would be less simply related to the fundamental rate constants. The model makes no assumption with regard to the physical nature of the sorption centers, and its success therefore contributes nothing to the solution of this problem.

Summary

An analysis of Burwell and Taylor's data on the activated sorption of hydrogen by chromium oxide has led to the derivation of a rate equation that fits the data for moderate amounts of sorption very well. The derivation is based on a simple model of the sorption process, involving primary adsorption followed by diffusion to secondary centers. This model also accounts, qualitatively at least, for the failure of the equation at extreme conditions.

PITTSBURGH, PA. RECEIVED DECEMBER 30, 1936

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[9] H. S. Taylor, *Z. Elektrochem.*, **35**, 542–549 (1929).

[10] A. F. H. Ward, *Proc. Roy. Soc.* (London), **A133**, 506–535 (1931).

[11] Adolf Smekal, *Z. Elektrochem.*, **35**, 567–573 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHERN MONTANA COLLEGE]

Acylselenoureas

BY IRWIN B. DOUGLASS

The investigation of the acyl isothiocyanates and certain acylthiourea derivatives by the author[1] and a review of certain organic selenium derivatives by Bradt[2] suggested the possibility that acid chlorides might react with metallic selenocyanates in a manner analogous to their reaction with the thiocyanates.

The work thus far accomplished indicates that there is a vigorous reaction when acid chlorides and KSeCN are brought together in acetone solution. In no case has the product (I) been

$$\mathrm{RCOCl} + \mathrm{KSeCN} \longrightarrow \mathrm{RCOCSeN}\ (\mathrm{I}) + \mathrm{KCl} \quad (1)$$

isolated and the evidence thus far accumulated does not definitely establish it as a selenocyanate, an isoselenocyanate, or an equilibrium mixture of the two. The fact, however, that (I) in acetone solution when treated with amines forms selenoureas according to reaction (2) indicates

$$\mathrm{RCOCSeN} + \mathrm{R'NH_2} \longrightarrow \mathrm{RCONHCSeNHR'} \quad (2)$$

that (I) must have the structure RCONCSe or at least must consist of an equilibrium mixture containing a large proportion in that form. On the basis of this evidence, the acyl derivatives resulting from the reactions between acid chlorides and potassium selenocyanate will be referred to as acyl isoselenocyanates or acylselenocarbimides.

This paper describes the properties of a few acylselenoureas prepared by reactions (1) and (2). The grouping RCO– was varied to include acetyl, carbethoxy, pyromucyl and benzoyl so as to gain some idea of the behavior of various acyl isoselenocyanates when treated with aniline, and the group R′ was varied to determine the behavior of benzoyl isoselenocyanate when treated with different amines.

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[1] Douglass and Dains, THIS JOURNAL, **56**, 719, 1408 (1934); Douglass and Forman, *ibid.*, **56**, 1609 (1934).

[2] Bradt, *J. Chem. Ed.*, **12**, 363 (1935).