

## **The application of temperature scanning to adsorption studies**

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Experimental studies of adsorption isotherms are less common than one would like, if we are to make sufficient data available to validate recent progress in the theory of adsorption. One reason for this state of affairs is the experimental difficulty and the length of time required to obtain satisfactory data using conventional methods of measuring adsorption rates and isotherms. In many systems these constraints on the availability of broad-ranging experimental data on adsorption can be eliminated by the use of a Temperature Scanning - Stream Swept Reactor (TS-SSR), a new technology to be described below. The TS-SSR is a "kinetics instrument", similar in its operation to the better known Temperature Programmed Desorption (TPD) apparatus, which operates in a way designed to yield "raw data" suitable for calculating isotherms and adsorption rates, without any presumptions regarding the behaviour of the system.

As I will show, a single TS-SSR "experiment", lasting perhaps eight hours, will produce a set of "raw data" which, after appropriate processing, will yield the kinetics of adsorption, the kinetics of desorption, and numerous isotherms for the system under study, all over a broad range of experimental temperatures. The experimental rate and isotherm data can then be used "as is", in which case no mechanistic interpretation is associated with the results but the results can still be used for equipment design purposes; or, it can be compared to appropriate rate and/or isotherm equations derived from theory or from intuitive postulates. In this presentation I will show how to acquire the "raw data" using a TS-SSR and make it yield all the kinetic constants, as well as their Arrhenius parameters, for an system involving Langmuirian adsorption kinetics and isotherms.

In order to give a full and generalized presentation of the theoretical treatment and experimental procedures used in a TS-SSR, I will make use of a simulation of a hypothetical adsorption-desorption system. To this end I will use a TS-SSR simulation available from SE Reactors Inc., the

developers of this technology, which will allow me to examine the results that would be obtained by a real TS-SSR, but over a wider range of reaction conditions than would normally be available in a real system. Real systems would generally require that the TS-SSR be specifically designed or configured to achieve such a wide range of operating conditions in any given system. However, even when using the more limited operating conditions that can be achieved in an available TS-SSR, one can generally get enough data to interpret the results in the manner described, albeit one may require supplementary information such as the monolayer coverage, obtainable from other sources, or from additional, more specialized experiments using the same TS-SSR.

## 1. INTRODUCTION

A TS-SSR consists of:

- a plug flow reactor in which the solid sample is placed;
- a heater/cooler capable of ramping the temperature of the reactor over the desired range of temperatures;
- and a detector which can measure the amount of adsorbate in the stream of carrier gas passing over the adsorbent.

Specific variants of this configuration can be readily envisioned, such as a reactor cooled below ambient conditions in order to access sub-ambient temperatures; various methods of exposing the sample to the sweeping gas; etc.

Operation begins with placing the sample of adsorbent in the reactor and sweeping it with a non-adsorbable carrier gas at a sufficiently high temperature to achieve complete desorption. Next, a desired level of surface coverage is achieved by introducing an appropriate concentration of adsorbate in the carrier gas, at a temperature at which the level of coverage corresponds to equilibrium with the adsorbate concentration used. Most often, as we will see, this amount is zero, and the experiment begins with a completely bare surface.

The initial temperature is adjusted in the presence of the sweeping stream of gas to a level at which the adsorbent is capable of adsorbing, and the adsorbate is introduced into the sweeping stream. Simultaneously, temperature ramping is initiated at a preselected rate. As the run time (clock time) progresses, the concentration of adsorbate at the outlet of the reactor is measured. In view of the need to measure the phenomena being observed at constant gas phase concentration, it is important that this quantity vary as little from the inlet value as possible. The flow of the carrier gas must therefore be adequately fast and the concentration measuring device must be sensitive to small concentration differences and free of random noise.

As temperature is ramped upward, the adsorbate concentration in the sweeping stream decreases at first, indicating that the surface is being covered

by adsorbate deposited from the sweeping stream at the low temperatures present in the beginning of the run. As time passes and the temperature continues to increase, we eventually reach a condition where the previously adsorbed material begins to leave the surface and the concentration of adsorbate in the sweeping stream rises above its entrance value. In the end, the entrance and exit values begin to converge, as the surface approaches the fully purged condition at the highest temperatures of the ramp.

The described procedure constitutes a single "run" in a temperature scanning "experiment". To complete the "experiment" the same procedure is repeated some ten times or more, each time using a different temperature ramping rate. The full set of runs, each at a different ramping rate, constitutes a TS-SSR experiment which can be used to yield the rates and isotherms for this system.

## 2. A TS-SSR EXPERIMENT: USING A FULLY COVERED SURFACE AT THE START

Let us first examine the case where the surface is initially fully covered, at some low temperature, in the presence of a suitable concentration of adsorbate in the stream of gas flowing over the solid. We simultaneously remove the adsorbate from the sweeping stream and begin to raise the sample temperature. In this situation we will observe the trace of change in the output concentration of adsorbate in the sweeping stream that we see in Figure 1. The absolute values of the change of concentration are kept as low as practicable by using a sufficiently rapid rate of sweeping-gas flow. This trace represents the result from one run of a TS-SSR experiment and need not consist of a single peak. If there are two or more types of adsorption sites, one could observe a peak with shoulders, or completely separated peaks, without changing anything in the methods of experimentation or interpretation to be described. The experiment will in all cases yield the net overall rates of adsorption or desorption. Only when we come to interpret the mechanism of the adsorption-desorption process would we have to postulate specific rate expressions for each of these processes on each of the sites.

In TPD studies, such experimental results are normally interpreted qualitatively. Here we will show that, when complete TS-SSR experiments are done in the prescribed way, they can be used to yield quantitative kinetic data. Although the requirements for performing a proper TS-SSR experiment are more strict than those necessary for a satisfactory TPD run, the advantages to be gained by taking this trouble are large.

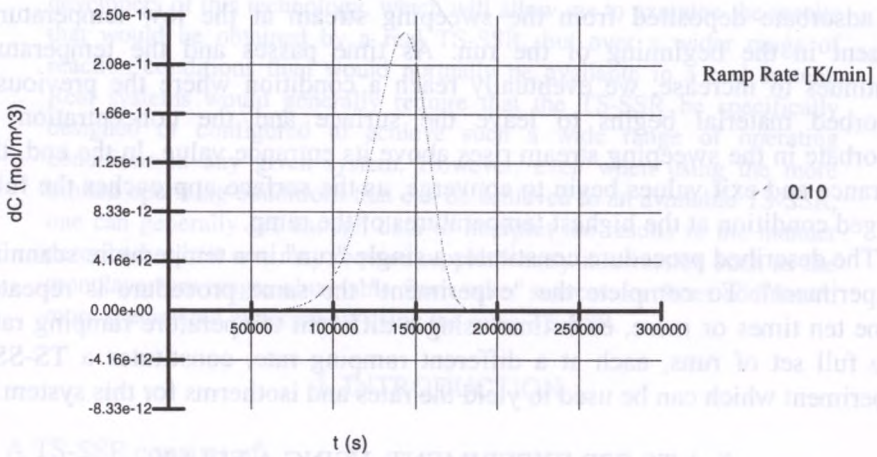


Figure 1. Concentration change vs clock time for various ramp rates

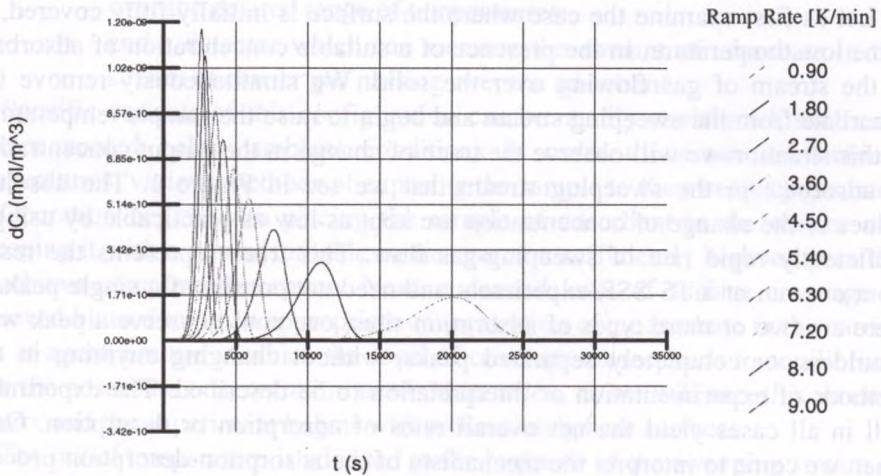


Figure 2. Concentration change vs clock time for various ramp rates

Figure 1 shows a single desorption run, from a sample of adsorbent initially fully covered by adsorbate. The sweeping stream contains no adsorbate and consists of inert gas only. The plot of delta concentration vs. time on the temperature ramp shows a simple peak which corresponds to desorption from an energetically homogeneous surface.

If the ramping operation is repeated on the same sample, starting from the same initial condition but varying the ramping rate with each run, we will obtain the results shown in Figure 2. There the results of the run with the

slowest ramping rate are those which yield the slowest most protracted curve shown.

Notice that in each run the total amount of adsorbate driven off is represented by the area under the curve. Thus the area under each curve in Figure 2 should be the same if no poisoning by un-desorbable species takes place in each cycle of adsorption-desorption on the same sample. If the sample must be replaced from run to run, the several runs of an experiment can be made compatible by renormalizing their areas to a common value. In either case the areas under the curves offer important information about the relationships between runs in an experiment.

Notice also that, if the surface had been fully covered at the start, as we have postulated, the integral under the curve up to a given time, divided by the total area under the curve, is the fraction of surface uncovered by the desorption. In cases where the surface is not fully covered at the start, appropriate changes to the procedure we are about to describe must be made. These normally require measurement of the "monolayer capacity", defined in some suitable way, and obtained in a separate experiment.

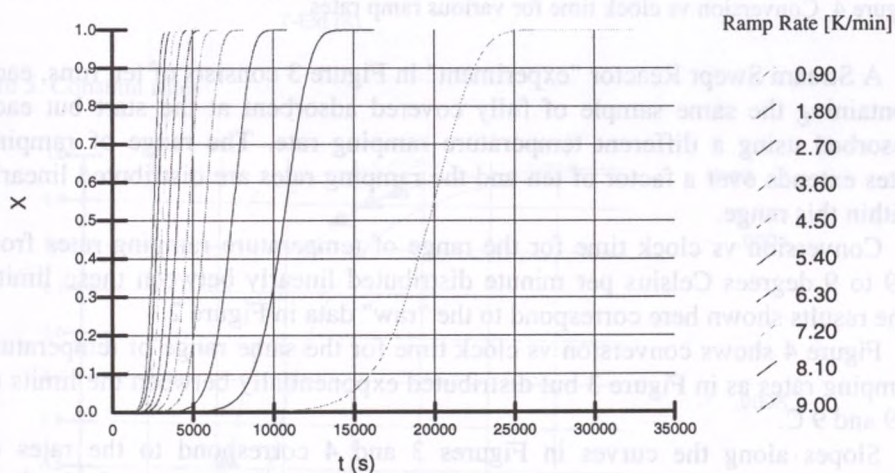


Figure 3. Conversion vs clock time for various ramp rates

Figure 3 shows the curves of conversion vs. time obtained in this way using a linear distribution of temperature ramping rates over a range spanning a factor of ten. Figure 4 shows the same system with the ramping rates distributed exponentially over the same range of rates. Obviously the exponential distribution results in a more uniform distribution of data over the range of conditions studied and is to be preferred in practice. In applying temperature scanning methods, it is frequently found that exponential distributions of the

variable that is changed between runs give the most even coverage of the region being scanned.

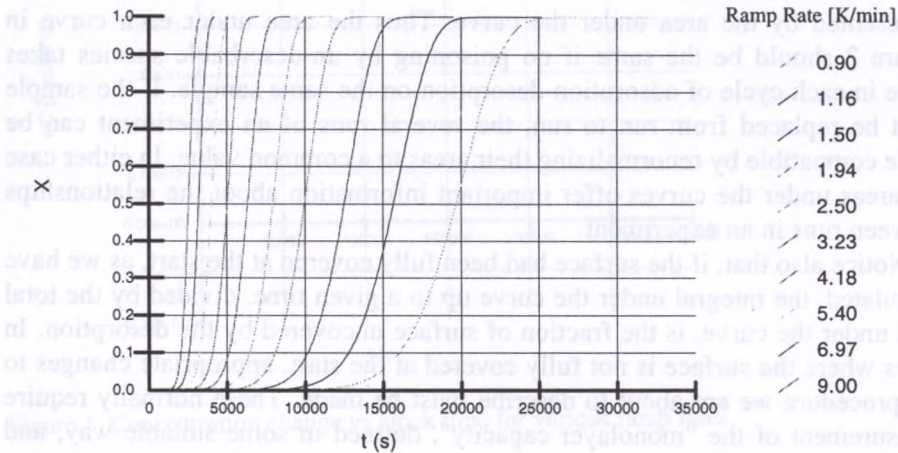


Figure 4. Conversion vs clock time for various ramp rates

A Stream Swept Reactor "experiment" in Figure 3 consists of ten runs, each containing the same sample of fully covered adsorbent at the start but each desorbed using a different temperature ramping rate. The range of ramping rates extends over a factor of ten and the ramping rates are distributed linearly within this range.

Conversion vs clock time for the range of temperature ramping rates from 0.9 to 9 degrees Celsius per minute distributed linearly between these limits. The results shown here correspond to the "raw" data in Figure 2.

Figure 4 shows conversion vs clock time for the same range of temperature ramping rates as in Figure 3 but distributed exponentially between the limits of 0.9 and 9 C.

Slopes along the curves in Figures 3 and 4 correspond to the rates of desorption, since they represent the rate of change in the amount of adsorbent being swept from the sample. A plot of these slopes will be identical in shape to Figures 3 and 4. Therefore, the "raw" data obtained by measuring the amount of adsorbate in the reactor effluent is a scaled representation of the rate of reaction. Each point along the raw data curve reports a rate (multiplied by a scaling factor involving the flow rate of the sweeping stream) at that coverage and at the pertinent temperature. By selecting from these data those points where the rate has some chosen value, one collects an isokinetic data set consisting of triplets of measured constant rate – temperature – conversion. A number of such data sets are shown in the reaction phase plane of conversion vs temperature on Figure 5. Figure 6 shows these rates fitted to the

corresponding isokinetic rates derived from the rate expression describing Langmuirian desorption.

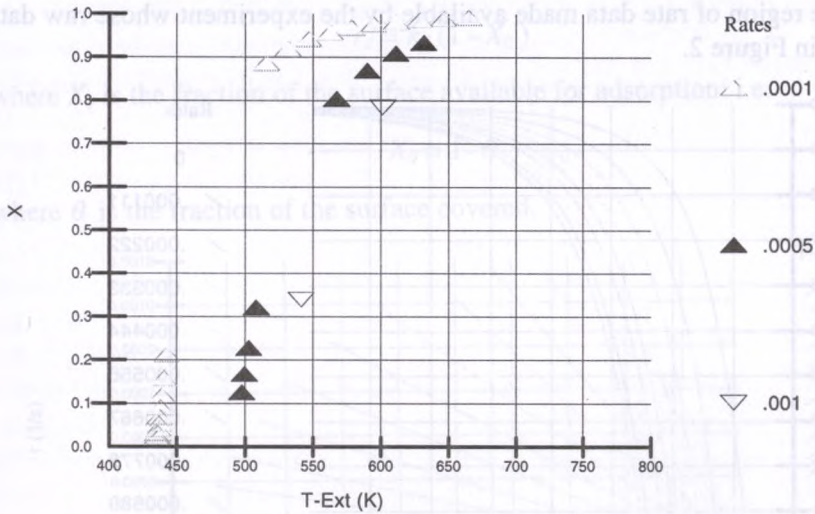


Figure 5. Constant rates

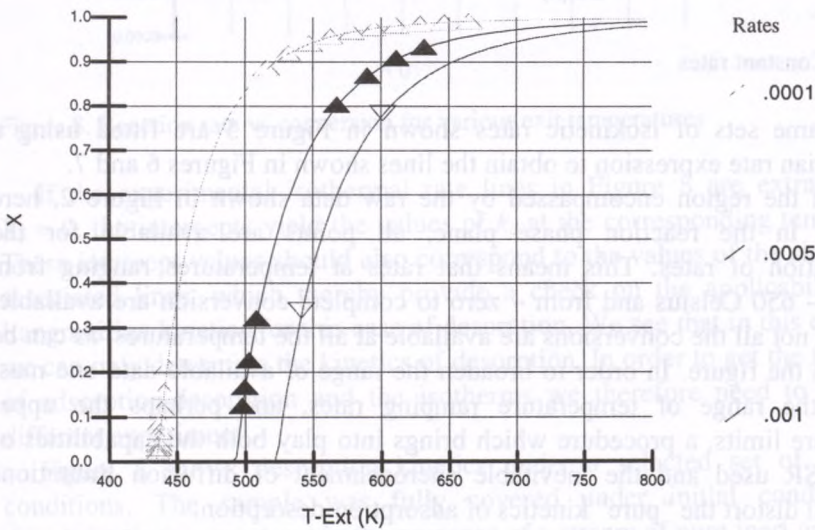


Figure 6. Constant rates

The essence of all temperature scanning methods is that one can obtain as many points, within the region of variables scanned, as one may wish. In principle, every point within this region is available. With this wealth of data the fitting of

theoretical rate equations is more certain, and the kinetic parameters obtained are more precisely defined than those available from the more limited data, scattered by experimental error, obtainable using traditional methods. Figure 7 shows the region of rate data made available by the experiment whose raw data is shown in Figure 2.

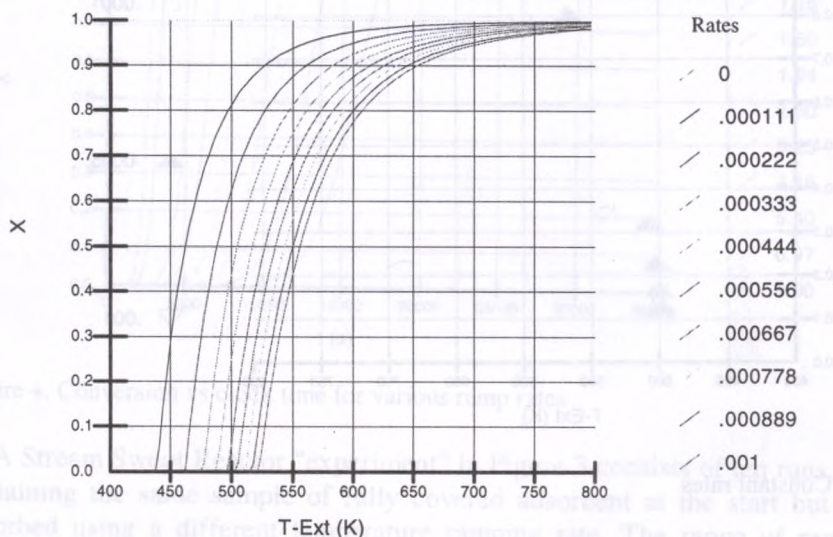


Figure 7. Constant rates

The same sets of isokinetic rates shown in Figure 5 are fitted using a Langmuirian rate expression to obtain the lines shown in Figures 6 and 7.

Within the region encompassed by the raw data shown in Figure 2, here presented in the reaction phase plane, all points are available for the determination of rates. This means that rates at temperatures ranging from ~ 400 to ~ 650 Celsius and from ~ zero to complete conversion are available. However, not all the conversions are available at all the temperatures, as can be seen from the figure. In order to broaden the range of available data one must broaden the range of temperature ramping rates, and perhaps the upper temperature limits, a procedure which brings into play both the capabilities of the TS-SSR used and the inevitable encroachment of diffusion limitations which will distort the "pure" kinetics of adsorption-desorption.

Alternatively one can select, from the same set of data, sets of isothermal rates: that is, rates at the same temperature and whatever conversions may be applicable. Such sets of rates are shown in Figure 8.

Since the sample was initially fully covered by adsorbate, the rates at any one temperature decrease as coverage decreases, until they reach zero when the



sample is fully desorbed. Since desorption proceeds by a first order process in the Langmuirian postulates, the isothermal kinetics are linear and in the  $r_d$  vs  $X_0$  plane all rates fall along the straight lines:

$$r_d = k_d(1 - X_0)$$

where  $X_0$  is the fraction of the surface available for adsorption: i.e.

$$X_0 = 1 - \theta$$

where  $\theta$  is the fraction of the surface covered.

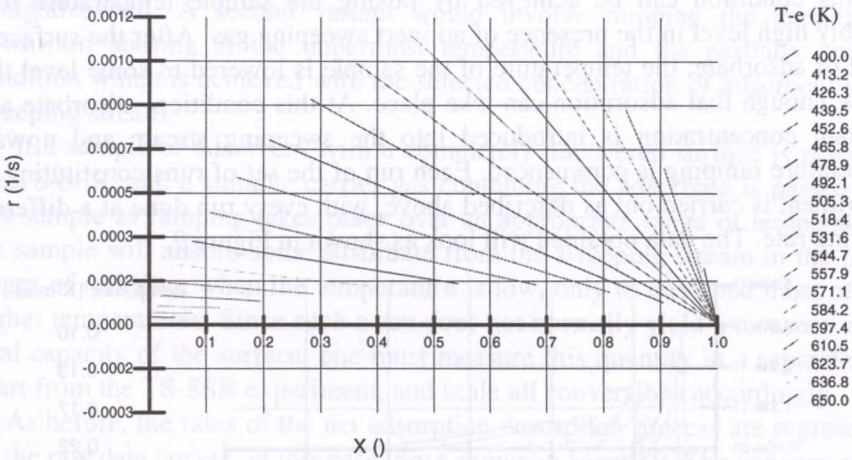


Figure 8. Reaction rate vs conversion for various exit temperatures

If the experimental isothermal rate lines in Figure 8 are extrapolated to  $X_0 = 0$ , the intercepts yield the values of  $k_d$  at the corresponding temperatures. These intercept values should also correspond to the values of the slopes of the associated lines, which thereby provide a check on the applicability of the Langmuirian kinetics for this case of desorption. We see that in this experiment we can only determine the kinetics of desorption. In order to get the full picture of adsorption-desorption and the isotherms we therefore need to perform a different experiment.

Figure 8 shows desorption kinetics under a selected set of isothermal conditions. The sample was fully covered under initial conditions and desorption was carried out in the presence of a stream of pure inert gas.

### 3. A TS-SSR EXPERIMENT: USING A FULLY UNCOVERED SURFACE AT THE START

In order to obtain the information necessary to establish the kinetics and isotherms for an adsorbent, one must set up an experiment which examines both the adsorption and the desorption processes. Such an experiment must start with the surface of the adsorbent less than fully covered. In this way both adsorption and desorption rates can be observed and measured. The extreme case, and perhaps the easiest procedure to apply in practice, is to start with the surface completely free of adsorbate.

This condition can be achieved by raising the sample temperature to a suitably high level in the presence of an inert sweeping gas. After the surface is freed of adsorbate, the temperature of the sample is lowered to some level that is low enough that adsorption can take place. At this condition, adsorbate at a constant concentration is introduced into the sweeping stream and upward temperature ramping is commenced. Each run of the set of runs constituting an experiment is carried out as described above, with every run done at a different ramping rate. The data obtained will look as shown in Figure 9.

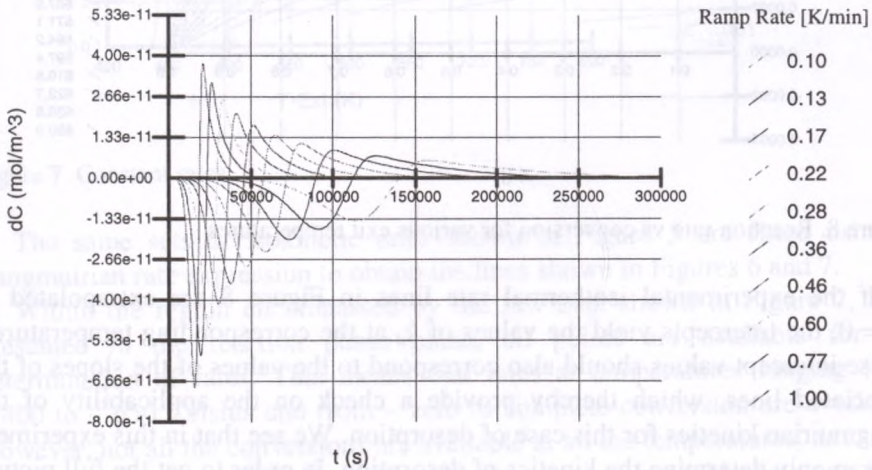


Figure 9. Concentration change vs clock time for various ramp rates

Notice that over the course of each run there is more material adsorbed than is desorbed, as shown by the fact that the negative area is larger than the positive. This is due to the fact that when desorption is essentially complete at the upper temperatures, the solid is still in the presence of a carrier containing some adsorbate and therefore cannot be completely free of adsorbate. One could continue to raise the temperature until there is no adsorbate left on the

surface, but the process of desorption is asymptotic with temperature and in principle would require an infinite temperature for complete desorption to be achieved. Best to stop short of that. In order to prepare the sample for the next run, one must switch off the adsorbate flow and wait at the high temperature until no more adsorbate appears in the effluent.

An important variant of this procedure is to achieve a preset level of coverage at the end of each run and start at that level in the next run. A TS-SSR experiment can be done starting at any well defined level of surface coverage as long as one knows the level at the start and the total surface capacity. The differences in data interpretation from those described here are trivial and straightforward. A second variant would involve ramping the temperature downward starting at the uppermost temperature and the partially covered condition which is achieved with the selected concentration of adsorbent in the sweeping stream.

If a sample of adsorbent with a completely uncovered surface is placed in the TS-SSR, and a suitable carrier gas containing the adsorbate is passed over this sample as ramping takes place over an appropriate range of temperatures, the sample will adsorb some adsorbate from the sweeping stream in the initial stages of ramping, when the temperature is low, only to desorb most of it at higher temperatures. Since such a run does not normally yield a measure of the total capacity of the surface, one must measure this quantity in a separate run, apart from the TS-SSR experiment, and scale all conversions accordingly.

As before, the rates of the net adsorption-desorption process are represented by the raw data curves, in this case those shown in Figure 9. The conversion-vs-time curves from which such rates are derived are shown in Figure 10. There we can clearly see that the surface is never completely covered nor completely stripped of adsorbate to bring it to its initial condition for the start of the next run.

From such data a selection of isokinetic rates can be made which, together with their Langmuirian fits, is shown in Figure 11.

The Langmuirian equation [1] for the net rate of desorption is given by:

$$r_d = k_d (1 - X_0) - k_a A X_0$$

$$r_d = k_d - (k_d + k_a A) X_0$$

or

$$r_d = k_d \theta - k_a A (1 - \theta)$$

Notice that the rate plots are again linear in the case of Langmuirian adsorption, facilitating the extrapolations which will be required to measure the isotherm values. More complex kinetics of adsorption-desorption will require more sophisticated data fitting, as well as careful selection of experimental conditions so that enough data is available to assure an adequate fit.

Conversion vs time plots of a run starting with a fully desorbed surface. Using the definition of conversion accepted here, the initial trend is to negative conversion as the surface is covered by adsorbate. Later, when the ramp temperature is high enough, conversion begins to increase as the surface is purged of adsorbate. The desorption never achieves 100% since there is always adsorbent present in the sweeping gas at the pre-set concentration.

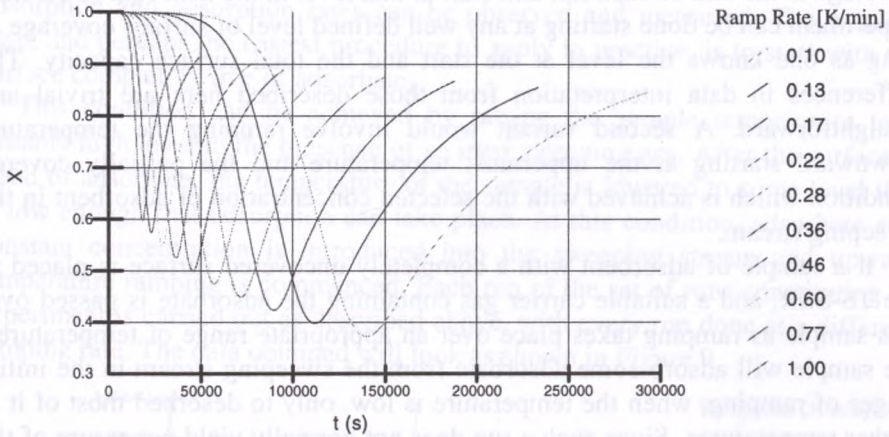


Figure 10. Conversion vs clock time for various ramp rates

Figure 11 shows the isokinetic rates measured, starting with a clean surface, include negative rates (those lying on the up-curving isokinetic lines on the left) and positive rates (those on the monotonically increasing curves on the right).

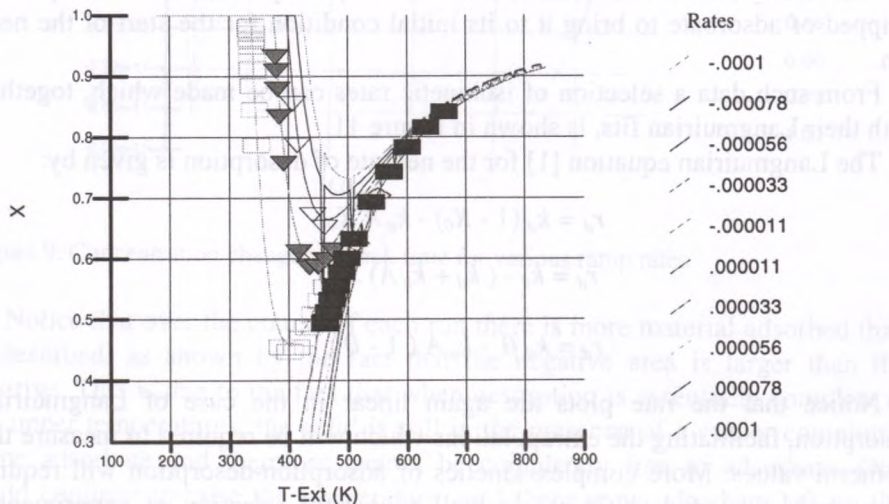


Figure 11. Constant rates

An alternative selection of rates can be made at constant temperature. As can be seen from the rate equations presented above, such isothermal rates can be expected to show linear behaviour as a function of conversion. Figure 12 shows that this is so. Various measurements which are available from Figure 12 reveal the kinetics and adsorption equilibria of this system.

To begin, it can be seen from the rate expression that when conversion goes to zero (i.e.  $X_0 = 0$  and coverage is complete) the straight lines extrapolate to the value of  $k_d$ . Since such values are available at a number of temperatures, one can obtain the Arrhenius parameters of  $k_d$ . As we saw previously, this will be so even if we do not start with a completely desorbed sample.

The slopes of the lines yield  $(k_d + k_a A)$  at the same temperatures and therefore, once we have established the values of  $k_d$ , the values of  $k_a$ ,  $A$  are available at a number of temperatures. This offers us an opportunity to calculate  $k_a$  if we know  $A$ , the concentration of the adsorbate in the sweeping gas. From this we calculate the Arrhenius parameters of the adsorption rate constant  $k_a$ .

We can now calculate the isotherm at any temperature from the values of  $k_a$ ,  $k_d$  and  $A$ .

$$X_0 = k_d / (k_d + k_a A)$$

$$1 - X_0 = k_a A / (k_d + k_a A) = \theta$$

$$\theta = K_A A / (1 + K_A A)$$

where  $K_A = k_a / k_d$  is the equilibrium constant for adsorption.

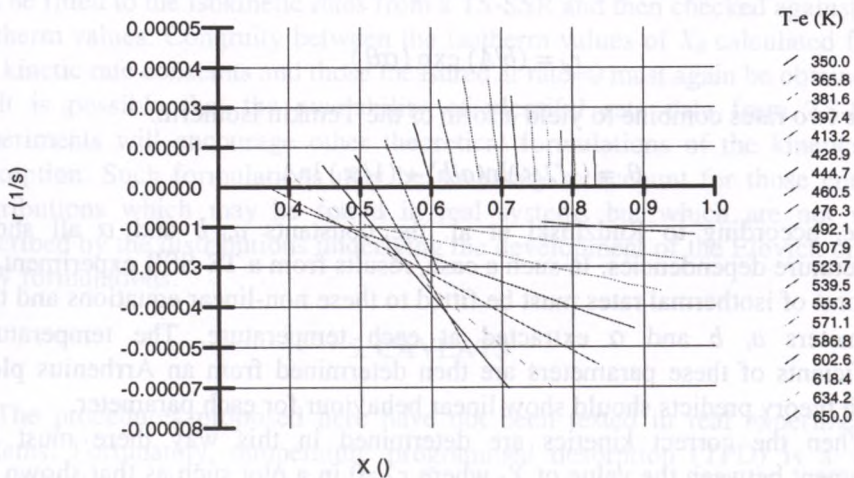


Figure 12. Reaction rate vs conversion for various exit temperatures

The isotherm values can be confirmed at each temperature by noting the value of  $X_0$  where the kinetic line cross the zero-rate level. At that point the isotherm should apply and the value for  $X_0$  read from the plot should be the same as that calculated from the equations given above.

Figure 12 gives a selection of net rates of desorption at a selection of constant temperatures from an adsorption-desorption experiment starting with a completely clean surface. Note that all the net desorption rates show linear behaviour since the net rate is :

$$r_d = -ka A X_0 + k_d (1-X_0) = k_d - (ka A + k_d) X_0 .$$

#### 4. NON-LANGMUIRIAN KINETICS

The above discussion was based on the supposition that the adsorption-desorption kinetics obey the linear equations appropriate for homogeneous surfaces. If on the real adsorbent used there exists a distribution of adsorption energies, more complicated kinetics will govern the adsorption-desorption rates. We can consider two such instances.

**Elovich kinetics.** There are numerous reports of an equation known as the Elovich equation:

$$r_a = (aA) \exp (-\alpha\theta)$$

applying to the rates of adsorption. Recently Rudzinski et al.[2] have shown that the reverse kinetics, those for desorption, in such a case must be of the form:

$$r_d = (b/A) \exp (\alpha\theta) .$$

These two rates combine to yield a form of the Temkin isotherm:

$$\theta = (1/2\alpha) \ln(a/b) + (1/\alpha) \ln A$$

where, according to Rudzinski et al. the constants  $a$ ,  $b$  and  $\alpha$  all show temperature dependencies. In such a case, results from a TS-SSR experiment in the form of isothermal rates must be fitted to these non-linear equations and the parameters  $a$ ,  $b$  and  $\alpha$  extracted at each temperature. The temperature coefficients of these parameters are then determined from an Arrhenius plot, which theory predicts should show linear behaviour for each parameter.

When the correct kinetics are determined in this way there must be agreement between the value of  $X_0$  where  $r_d = 0$  in a plot such as that shown as Figure 13, and the isotherm value of  $X_0$  calculated from the kinetic parameters. Here, as always, this redundancy provides a check on the validity of the rate parameters obtained from the kinetic correlations.

**Crickmore-Wojciechowski kinetics.** There is another, perhaps more general, kinetic formulation of the behaviour of adsorption on heterogeneous surfaces. It is based on the work of Kemp and Wojciechowski [3] which deals with the overall kinetics of reactions proceeding via sets of simultaneous, first order, parallel reactions whose rate constants were distributed in various ways. This is exactly the situation in adsorption on energetically heterogeneous sites with a distribution of adsorption energies. The overall net rate of adsorption in such a case is given by:

$$r_a = -k_d (1 - X_0)^{(1+W)} + k_a A X_0^{(1+W)}$$

which leads to an isotherm of the form:

$$X_0 = (k_d / k_a A)^{(1+W)} / (1 + (k_d / k_a A)^{(1+W)})$$

or

$$\theta = (k_a / k_d A)^{1/(1+W)} / (1 + (k_a / k_d A)^{1/(1+W)})$$

$$\theta = (K_a A)^{1/(1+W)} / (1 + (K_a A)^{1/(1+W)})$$

where  $W$  is the "heterogeneity parameter". For homogeneous surfaces  $W = 0$  and the isotherm reduces to that of Langmuir. As heterogeneity increases so does  $W$ .

Since the Langmuir equations are a special case of the more general Crickmore-Wojciechowski (C-W) equations [4], despite the plethora of isotherms, there are only two full sets of kinetically-based equations for describing adsorption: the Elovich set and the C-W set. These rate equations can be fitted to the isokinetic rates from a TS-SSR and then checked against the isotherm values. Congruity between the isotherm values of  $X_0$  calculated from the kinetic rate constants and those measured at rate=0 must again be obtained.

It is possible that the availability of plentiful rate data from TS-SSR experiments will encourage other theoretical formulations of the kinetics of adsorption. Such formulations may be necessary to account for those energy distributions which may be found in real systems but which are not well described by the distributions underlying the development of the Elovich or the C-W formulations.

## 5. CAVEATS

The procedures proposed here have not been tested in real experimental systems. Fortunately, temperature programmed desorption (TPD) is a well established procedure and there is much evidence that it can yield reproducible results. The TS-SSR combines well defined sets of data, similar to that available from a TPD apparatus, and uses the concept of data "sieving" to formulate a fresh approach to the interpretation of this data. This yields results

which are not available from conventional TPD operation. However, the similarity of the equipment and of the raw data to that found in TPD operation suggests that the methods proposed here will certainly be feasible. Further, the theory presented above is free of assumptions and approximations.

There are caveats to be noted, nevertheless. The principal one is the role of particle diffusion in adsorption studies. In the procedures described we set out to study the kinetics of adsorption. We do not want these to be distorted by mass- and/or heat-transfer processes if we are interested in the fundamentals of the adsorption-desorption process. This will require that particle size be reduced until heat- and/or mass-diffusion is not rate-limiting at any of the temperature conditions to be studied. Moreover, bulk (i.e. gas-phase) diffusion must be eliminated by the proper exposure of the solid to the fluid, be it gas or liquid. Workers who are accustomed to the measurement of equilibrium isotherms at steady state should beware of these new requirements. Whereas in measuring isotherms at steady state we can afford to wait until conditions line out, in TS-SSR operation we measure adsorption-desorption phenomena instantaneously and do not wait for steady state to be established.

These requirements of TS-SSR operation also differ significantly from the operating procedures found to be satisfactory in obtaining qualitative, or "semi quantitative", data from a TPD experiment. There reproducibility is important but it is often sufficient to observe qualitative differences in the shapes of signal peaks. In the TS-SSR we are not only interested in the quantitative details of the peaks but also plan to assign specific quantitative, mechanistic, interpretations to the rates of desorption they reveal.

Finally, even if diffusion limitations can not be entirely removed, there exists a possibility of determining the role of diffusion as a function of particle size. The requirement is to perform a series of identical experiments as described above but using different particle sizes in each experiment. This would allow extrapolation of quantities measured on each particle size to zero particle size, where the diffusion-free quantity would be determined and used to examine the diffusion-free kinetics of the system. Such data would also yield a function describing the influence of diffusion (or particle size) on desorption kinetics. In practice, where the adsorbent may have to be applied at a particle size dictated by engineering considerations, such measurements, even if correlated on an empirical basis, will provide valuable information for the design of industrial systems.

There is also an opportunity to study the interactions of gas mixtures. In principle any inert gas used as the sweeping stream should give the same kinetics and isotherms for the adsorbate under study. To the extent that this is not so, one has to conclude that the carrier gas interacts with the adsorbent and/or adsorbate. This presents an opportunity to study the competition for sites, or other interactions which may be postulated in such cases. Since a TS-



SSR experiment is relatively quick and easy to carry out, thorough studies of a wide variety of competitive adsorption systems can be contemplated.

## 6. CONCLUSIONS

Fairly simple apparatus using temperature scanning in its operation can yield a great deal of information about the kinetics and thermodynamics of adsorption in any system, regardless of its complexity. A properly designed Temperature Scanning Stream Swept Reactor (TS-SSR) can produce enough data to ascertain the rates of adsorption and of desorption, and the equilibrium isotherms, over a range of temperatures and surface coverages, in about eight hours of operation.

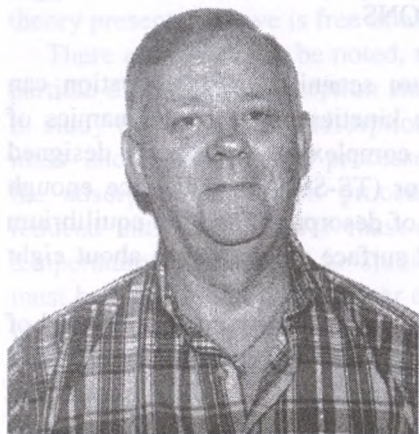
The effects of particle and/or bulk diffusion, competitive adsorption, and of gas phase adsorbate concentration can be examined by repeating the TS-SSR experiment using various experimental conditions. Since a TS-SSR experiment should normally take no more than a day of largely, or even fully automated operation, one can envision undertaking thorough investigations of phenomena considered too complicated to study by conventional methods.

In particular, the determination of the kinetics of the adsorption-desorption process, in parallel with commensurate measurements of adsorption isotherms, promises to yield much needed experimental data on surface energetic heterogeneity, and on the thermodynamics of adsorption in general.

## 7. REFERENCES

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## CURRICULUM VITAE

**Prof. Bohdan Wiesław Wojciechowski.**

Born in Wilno, Poland in 1935. In 1941 he was transported to Kazakstan. From there he travelled via Tehran and Alexandria to Scotland, where he attended elementary and secondary school. He received both Scottish and Polish secondary school graduation diplomas.

In 1952 he emigrated to Canada. He received a B. A. Sc. in 1957 and an M. A. Sc. in 1958 in Chemical Engineering, both from the University of Toronto. In 1961 he received a PhD in Chemistry from the University of Ottawa.

Following a Post Doctorate at the National Research Council he accepted a position as Senior Research Chemist with Mobil Oil in Paulsboro New Jersey USA in 1962.

Dr. Wojciechowski taught Chemical Engineering at Queen's University in Kingston Canada from 1965 until 1996, and was appointed full professor in 1972. He was named Professor Emeritus in 1996, and continues with research and publication. Since 1993 he has also been President of SE Reactors Inc. His research interests focus on kinetics and catalysis, and he has authored or co-authored over 170 refereed publications in these fields, as well as four review papers and two textbooks. He has lectured and/or consulted in more than 100 universities and laboratories in over 40 countries.

Professor Wojciechowski has made a succession of significant contributions in kinetics and catalysis, starting with his Ph. D. work which resolved long-standing questions regarding the action of inhibitors in pyrolysis reactions, and moving on to research related to hydrocarbon conversion and catalysis. His hydrocarbon studies have ranged from pure hydrocarbon reactions to multi-component reactions in the presence of catalyst decay. In 1992 he received the Chemical Institute of Canada's Award in Catalysis in recognition of his overall contributions to the field of catalysis research.

While working in the petroleum industry his interests shifted from homogeneous hydrocarbon conversion to catalytic studies. Shortly after joining Queen's University in 1965, Professor Wojciechowski proposed his now well-established Time on Stream theory of catalyst decay. This concept, which began the establishment of a mathematical foundation for the field of catalytic cracking, was extended by the addition of Optimum Performance Envelopes which he introduced a few years later.

With the combined power of these two concepts, as well as other contributions such as the "refractoriness effect", all applied in a program of uniquely systematic, mathematically-rigorous, consistent and thorough studies, he and his colleagues have made a series of significant advances in the understanding of catalytic systems; the most recent is the Chain Mechanism concept of catalytic cracking. The cumulative nature of his work is demonstrated by the fact that many of the concepts developed in his Ph. D. research on gas-phase inhibition continue to be fundamental to his contributions to understanding the complexities of catalytic cracking.

Among his other areas of research, Professor Wojciechowski has contributed a new and versatile isotherm to the field of adsorption on heterogeneous surfaces, and was involved in a definitive study of the kinetics of Fischer-Tropsch and other synthesis reactions; the findings from this latter work were collected and published in two review articles.

Professor Wojciechowski's research has concentrated on building a soundly-based, systematic and consistent body of knowledge on the formation and rearrangements of hydrocarbon molecules. It has therefore been of interest not only to academic colleagues but also to researchers in applied fields such as catalyst manufacturing, transportation fuels, petrochemicals, and other catalytic applications including environmental protection.

Drawing on this body of knowledge, and in particular on recent advances made by his group in understanding the mathematics of catalytic reactions, he has developed the Temperature Scanning Reactor (TSR), which abandons the conventional isothermal paradigm for studying catalytic and non-catalytic reaction processes. This breakthrough promises to increase research productivity for both academic and industrial applications by factors of hundreds and even thousands. The TSR methodology has been patented by Queen's University, and is available to other researchers through SE Reactors Inc., a company established by Professor Wojciechowski for this purpose.

