USE OF TRACERS IN STUDYING THE MECHANISM OF CATALYTIC REACTIONS. FINAL REPORT, JULY 1957--JULY 1971

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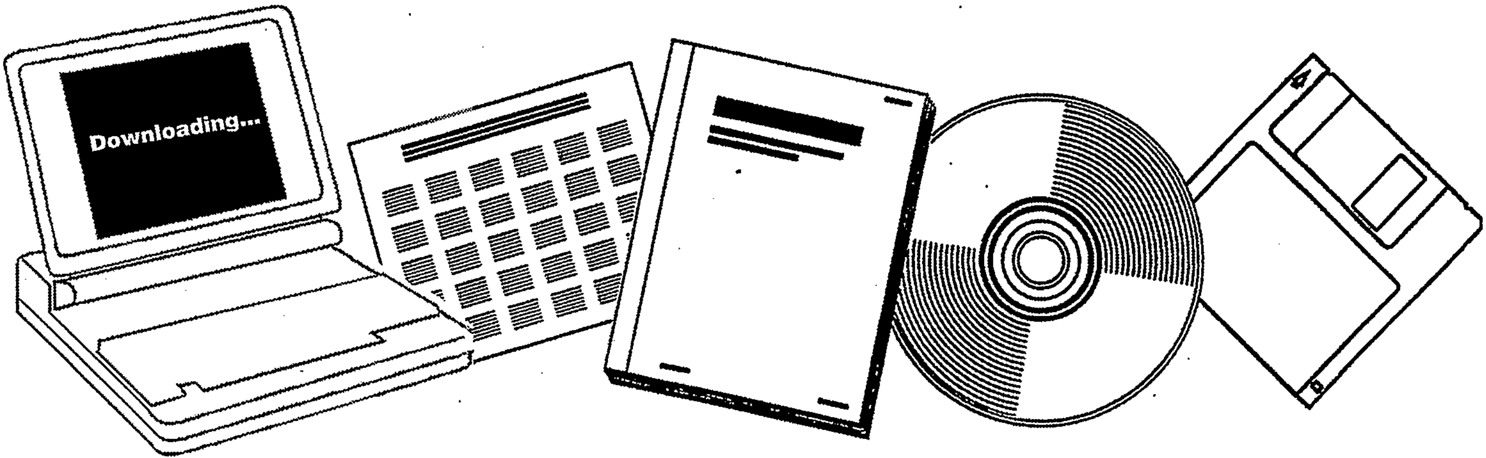

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Final Report on Contract AT(11-1) - 3273
The Use of Tracers in Studying the Mechanism of Catalytic Reactions

The Johns Hopkins University
Baltimore, Maryland
July, 1957 to July, 1971

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The present final report gives a brief summary of the research results obtained during the period July, 1957 to July, 1971. They have been published in part in a series of 15 papers listed in the references. An additional seven are still in the process of being written and will, it is hoped, be published later.

The work and accomplishments of this fourteen-year period may, for convenience, be grouped under the following seventeen headings; grouped, for convenience, into four main headings:

- Catalytic Cracking and Cracking Catalysts
  - Secondary reactions--tracer studies over silica-alumina catalysts
  - Secondary reactions in cracking hexadecane over catalysts containing zeolites
  - Secondary reactions in cracking hexadecane over zeolite catalysts
  - Effect of water vapor on adsorption and cracking of hydrocarbons
  - Free radical cracking
  - Adsorption of CO, N_2, Kr on exchanged and heated zeolites
  - Ethylene hydrogenation over cracking catalysts vs. pentene formation on cracking pentane
  - Cracking of low mol. wt. hydrocarbons
- Iron Catalysts for Ammonia Synthesis
  - Promoter content as revealed by $H_2{}^{18}O$ exchange and CO chemisorption
  - Influence of nitrogen chemisorption on CO chemisorption on unpromoted iron catalysts
  - Synthesis of hydrocarbons from CO and H_2 over iron catalysts
- Equation of State Work
  - Equations for relating vapor pressure to temperature for N_2, A, CO_2, H_2O and Ne.
- Miscellaneous
  - Mo_2C-Mo-C thermodynamics
  - Chromatographic separation of HD, D_2 and H_2
  - Dehydrogenation and dehydration of isopropyl alcohol
  - Chromatographic separation of NO and NO_2

The principal findings under each of these topics will now be summarized briefly together with a list of references in which the details of the work are given.

Catalytic Cracking and Cracking Catalysts

1. The study of secondary reactions in the catalytic cracking of hexadecane over silica-alumina catalysts by using carbon-14 tracer compounds.

For many years those who have constructed detailed mechanistic pictures of the catalytic cracking of hydrocarbons over silica-alumina catalysts have been forced to guess as to the extent to which the initial cracking products take part in secondary reactions leading to some final product distribution. By using radioactive olefins, paraffins and aromatics added in tracer amounts to a stream of hexadecane being passed over a cracking catalyst we have been able to obtain a much more quantitative picture as to the secondary reactions taking place. Our findings may be summarized as follows:

a. Paraffins added as tracers(1)(2)(5) include propane, n-butane, heptane, and dodecane. None of them built in appreciably to form higher molecular weight compounds. It may be assumed therefore that paraffins formed as primary cracking products for the most part appear in the final products.

b. Olefins such as propylene, butene and pentene build in extensively(12)(13)(14) to form secondary products. The higher hydrocarbon paraffins, olefins and aromatics are all 30 to 50% as radioactive as the added olefin tracer in the exit gas. A paper now in the process of being written(18) puts these results on a quantitative basis. Runs were also made using heptene as a tracer but the decomposition of the tracer into C_3 and C_4 compounds was so rapid that the behavior of the heptene molecule itself was difficult to follow.

All modern carbonium ion mechanism theories for catalytic cracking have emphasized that C_2 molecules are ordinarily not produced in catalytic cracking. This suggested that added ethylene tracer would not be incorporated into higher molecular weight compounds. Experiments proved this to be the case. Except for a small percent conversion to ethane, the ethylene passed through(4)(17) the cetane cracking unchanged.

c. Benzene and toluene formed small amounts(4)(5)(17)(18)(20) of C_7 to C_{10} aromatic products but these were negligible in amounts. Only two alkylations were outstanding, namely the formation of cumene from benzene and the formation of para-cymene from toluene, both by alkylation with propylene. These products were 50 to 90% as radioactive as the parent tracer molecules in the final products.

d. Coke formed during a cracking process is inactive(2) in the sense that the carbon it contains does not transfer to compounds being formed or cracked on the partially coked catalyst.

e. When pentene-1 is added as a tracer the distribution of the carbon-14 shows(19) that rapid equilibration to the C_5 olefin isomers takes place.

f. The formation of aromatics does not appear to take place as a result of dehydrocyclization over the cracking catalyst during the cracking process.(4)(5)(17) This was demonstrated by showing the absence of C_7 and C_{10} aromatics when heptane and decane were added as tracers. Presumably the aromatics arise from a polymerization of C_3, C_4 and C_5 olefins among themselves to form cyclic compounds which dehydrogenate to aromatics.

g. The rate of normal butane-isobutane isomerization(1)(16) is very small under the conditions (372°C, 12 seconds time of contact) required to crack 30 to 50% of the cetane.

h. The order in which various compounds react with cracking catalysts to form coke was established by adding tracer compounds(4)(17) and noting the relative radioactivity of the coke. The paraffins form little coke; the aromatics are worse coke formers than the paraffins, and the olefins for a given molecular weight are at least ten times as active in forming coke as the paraffins. Among the paraffins coke forming tendencies increase 10 to 15 fold in going from propane to hexadecane.

i. The introduction of temperature sensitive terms into the standard Greensfelder method of calculation of product distribution and the use of experimental radioactive tracer results to correct for secondary reactions enables one to obtain fairly good agreement(3)(16) between the observed and calculated distribution for cracking hexadecane over a silica-alumina catalyst at 372°C.

j. Experiments with small beds(3)(16) of catalyst suggest that the catalyst at the entrance to a catalyst bed may have most of its active sites covered with adsorbed protons rather than with carbonium ions. The evidence suggests that the protons are less effective than the small carbonium ions in reacting with cetane to form cetyl carbonium ions.

2. Carbon-14 tracer studies of the secondary reactions in the catalytic cracking of n-hexadecane over silica-alumina and over catalysts containing zeolites.

Dr. Burton H. Bartley(18) extended the basic theory of interpreting tracer results in terms of specific participation of various cracking products in promoting further cracking. He worked primarily with radioactive butene-1, heptene-1 and toluene. This work is in the process of being written up for publication. It is available in detail in the dissertation of Dr. Bartley at the Johns Hopkins University, 1966. A compact summary of his principal results may be taken directly from the "summary" in his thesis as follows:

"The importance of secondary reactions in the catalytic cracking of n-hexadecane can be determined by a tracer method. The ratio of the amount of a particular product formed from a particular intermediate to the total amount of the particular product formed from the n-hexadecane is the quantity PC_a/PC given by the equation

$$\frac{PC_a}{PC} = \frac{\alpha_T^P(\text{obs})}{\alpha_T^P(\text{max})}\left[1 + \frac{PT}{PC}\right] - \frac{PT}{PC}$$

All quantities on the right-hand side of the equation are determined experimentally except $\alpha_T^P(\text{max})$. $\alpha_T^P(\text{max})$ is calculated on the basis of the kinetics and chemistry of the reactions. The $\alpha_T^P(\text{max})$ values vary widely depending upon the reactivity of the tracer and its abundance. For n-heptane, n-decane, benzene, and toluene tracers the $\alpha_T^P(\text{max})$ values are accurately determined. For ethylene and heptene-1 tracers the $\alpha_T^P(\text{max})$ values are determined within a factor of two. For propane and n-butane tracers the $\alpha_T^P(\text{max})$ values are determined within a factor of three. For the propylene, butene-1, and pentene-1 tracers the α_T^P(max) values are determined within a factor of five.

The n-hexadecane diluted with helium cracks to the extent of 34.55% over a silica-alumina catalyst at 372°C and a contact time of 5.1 seconds. The cracking increases to 77.0% when the catalyst is replaced with a molecular sieve catalyst and the contact time is increased to 8.0 seconds. A larger proportion of the products from the molecular sieve catalyst runs are high molecular weight compounds. Over twice as much coke per 100 moles of n-hexadecane cracked is formed over the molecular sieve catalyst. Many of the olefin compounds which show up as products over the silica-alumina catalyst appear to have been hydrogenated over the molecular sieve catalyst. The C_4 and probably the C_5 olefins are no longer equilibrated when the molecular sieve catalyst is used.

The butene-1 is important in the production of almost all products, although it is of less importance over the molecular sieve catalyst than over the silica-alumina catalyst.

The heptene-1 tracer is very reactive but does not play a very important part in the formation of products because it is present in such small amounts. Over half of the radioactivity from the added heptene-1 ends up in the i-butane molecules. The heptene-1 molecule probably rearranges after it becomes a surface carbonium ion to form a 2-m. hexyl carbonium ion. This carbonium ion then undergoes beta scission and after hydrogenation, propylene and i-butane are the resulting products. The radioactivity is in the first position of the heptene-1 molecule so all of it ends up in the i-butane in the above process.

From the butene-1 and heptene-1 results it is seen that even though a molecule is very reactive, it must also be present in large quantities if it is to play a significant role in the formation of products.

Even though the molecule itself is not very important in the quantity of product it yields, the carbonium ions which the tracer forms may still be of great importance in the formation of the products. The tracer technique can only determine the importance of the gaseous molecules of the intermediate and may tell nothing about the importance of the carbonium ions formed by the intermediate. Thus, when the carbonium ion of the intermediate is formed from some other substance, if the carbonium ion does not desorb and equilibrate with the intermediate in the gas phase before it reacts, then the tracer method will not be able to detect it.

Even though it is more reactive, butene-1 is not as important an intermediate in the formation of products over the molecular sieve catalyst as over the silica-alumina catalyst because less of the intermediate is present. On the other hand, the toluene is more important as an intermediate in the formation of products over a molecular sieve catalyst than over the silica-alumina catalyst because much more of the toluene reacts over the former catalyst, but the amount of toluene is the same over both catalyst.

The application of the PC_a/PC equation to all of the data collected to date leads to the following conclusions: The n-paraffins increase in activity with increasing molecular weight, but their importance as intermediates stays roughly the same. This is because the increase in activity of the n-paraffins with increasing molecular weight is offset by the decrease in abundance with increasing molecular weight. Olefins are by far the most important intermediates. Probably the most important intermediate is propylene because of its great abundance and moderately great reactivity. Butene and pentene each as a group rival propylene. The tracer studies on the molecular sieve catalyst along with the calculations of the α^{P}_{T}(max) values have shown that the carbonium ions may undergo several reactions before leaving the catalyst surface. Very little of the alkyl aromatic compounds are formed by the alkylation of benzene or toluene. The C_3, C_4, and C_5 olefins are the most important intermediates in the formation of the alkyl aromatic compounds."

3. Carbon-14 tracer studies of the secondary reactions in the cracking of hexadecane over zeolite catalysts(20).

Dr. John Bordley completed his dissertation in 1972(20) on the subject listed above as a heading for this paragraph. It is being written up for publication and should be published this year. Briefly the object of his work was to ascertain whether olefins and other molecules undergo secondary reactions in the cracking of cetane over zeolites. Two tracers were used, radioactive propylene and radioactive toluene. The zeolites are many fold as active as the amorphous silica-alumina catalysts and in general are more effective hydrogen transfer agents than the silica-alumina catalysts. They produce fewer olefins and more paraffins than the silica-alumina. It was expected therefore that the build in of tracer additives during the cracking might be very different on the zeolites as compared to the amorphous silica-alumina catalysts.

The results from the cracking runs over zeolites using propylene tracer showed that incorporation of radioactivity into other products was only about 1/10th as great as on the silica-alumina catalysts. This raises the question as to whether inherently the olefins formed by cracking over the zeolites are less inclined to undergo secondary reactions to form higher hydrocarbons. The other possibility is that the tracer propylene does not diffuse into the narrow pores of the zeolites sufficiently rapidly to equilibrate in an adsorption sense with the propylene being formed by the cracking. Unfortunately the data do not differentiate between the two hypotheses though we are inclined to believe that the slowness of equilibration of the radioactive propylene with the propylene formed by cracking is the cause of the low incorporation of the tracer propylene.

We had hoped that tracer experiments with radioactive toluene would help to decide whether the slow entrance of the tracer molecules into the zeolite cages was a controlling factor. Unfortunately the toluene results are rather indecisive.

Only a small fraction of the toluene was incorporated. The build-in of the tracer toluene was definitely not lower on the zeolites than on the silica-alumina catalysts and was perhaps a little larger. The work should be extended to other molecules intermediate in size between propylene and toluene.

4. The influence of water vapor on the adsorption and cracking of hydrocarbons (5) (21)

Previous work had shown that the addition of small amounts of water vapor to a silica-alumina cracking catalyst would increase the rate of cracking as well as the rate of isomerization of saturated hydrocarbons. However the addition of water vapor did not increase the chemisorption of isobutane, nor did it increase the rate of chemisorption or desorption. It was decided to attempt to obtain more definitive information by studying the effect of water vapor addition on the extent of chemisorption and the rate of cracking of one and the same hydrocarbon, namely heptane. The influence of water vapor on the cracking and isomerization of 223 trimethyl butane (triptane), and 2-methyl heptane was also measured.(5)(21)

The cracking and isomerization of the triptane was measured at 102, 160 and 200°C; the cracking and isomerization of 2 methyl pentane at 100°C; and the isomerization and cracking of heptane at 151, 200, 250, and 300°C. The optimum amount of added back water vapor was in the range 0.05 to 0.15%; the increase in the rate of cracking at the optimum water addition was about five fold. The isomerization of 2-methyl pentane increased twenty fold.

The radioactive adsorption experiments using n-heptane -1-^{14}C at 10 torr and a temperature of 110°C confirmed three types of chemisorption, namely, instantaneously exchangeable chemisorption (type 1), slowly exchangeable (type 2) and non-exchangeable (type 3). The amounts of slowly exchangeable chemisorption (type 2) and the non-exchangeable type both decreased with the addition of water vapor. On the other hand, the amount of type 1 adsorption increased moderately with an increase in the added water vapor. However the increase in type 1 is not as great as the increase in the cracking rate. Possibly, however, the evacuation at 110° used to differentiate between chemical and physical adsorption might have removed some of the type 1 adsorption. Nevertheless it must be admitted that at present we still do not have a good idea as to the manner in which water vapor alters the activity of a cracking catalyst for cracking or isomerizing hydrocarbons.

One other interesting observation in these experiments should be mentioned. Usually it is considered very difficult to isomerize n-hydrocarbons to those having quaternary carbon atoms. In one six-hour experiment on the isomerization of normal heptane it was noticed that all of the isomers were formed including 22- and 23-dimethyl pentane and 223 trimethyl butane. These latter three compounds constituted only about three percent of the isomerization products.

5. The free radical cracking of n-Butane.(7)

a. In some preliminary experiments that preceded some tracer runs on the catalytic decomposition of low molecular weight hydrocarbons (propane, butane and pentane) some runs were made in which in a circulating system the butane reactant was passed over mercury perchlorate to absorb the olefins. To our surprise the presence of the mercury perchlorate trap caused a large increase in reaction rate and a switch to methane as the principal product. It was at first thought that the removal of olefins was making possible the development of methyl carbonium ions on the catalyst surface. More extended work(7) using a flow system demonstrated that the mercury perchlorate is capable of reacting with propane or butane at room temperature forming free radicals which when carried into the reaction furnace at 450°C caused the thermal cracking of the hydrocarbons to increase abruptly in rate by as much as five fold. The enhancement was obtained even in the absence of a catalyst in the reaction vessel-the latter being filled with glass beads.

b. The products formed were those to be expected from thermal decomposition, two-thirds of the product consisting of equal quantities of methane and propylene, and one-third consisting of equal amounts of ethylene and ethane. It should be added that the passage of butane for a number of hours over the mercury perchlorate accumulated enough active material in a glass bead mixing tube so that when the latter was exposed to oxygen in the absence of gaseous butane a violent explosion occured. The nature of the free radicals or the active deposit was not ascertained.

6. Adsorption of N_2, CO and Kr on ion exchange silica-alumina cracking catalysts(8)

a. Recently Stone and his coworkers discovered that a sample of Faujasite that has been ion exchanged with calcium ions displayed a strong adsorption for carbon monoxide at 25°C and one atmosphere pressure. The adsorption in the big cages of the zeolite corresponded to one adsorbed carbon monoxide for each calcium ion. The heat of adsorption was about 12 kcals per mole of carbon monoxide. Since silica-alumina catalysts apparently possess acid sites that are very similar to those in zeolites it seemed worthwhile to study the adsorption of CO both before and after exchanging the acidic protons with calcium ions.

b. Unexchanged silica-alumina cracking catalysts dried by evacuation at 250°C showed normal physical adsorption for carbon monoxide, nitrogen, argon and krypton. The isotherms obeyed Henry's law and corresponded to a coverage of between one the two percent of a monolayer at 25° and one atmosphere pressure. The samples that were ion exchanged with calcium showed adsorption isotherms for CO at 25° that were still linear with pressures but had absolute values about three times as large as the unexchanged samples.

c. Evacuating the samples at 450°C caused increased adsorption for both the unexchanged sample and for the one exchanged with calcium ions. All of the isotherms for these samples were concave toward the pressure axis. The adsorption values at 100 torr were about three times as large for both the exchanged and unexchanged samples as on those evacuated at 250°C.

d. Evacuation of the samples at 800° increased the heats of adsorption to about 15 kcals per mole for both the exchanged and the unexchanged samples. The adsorption isotherms were in fact almost identical for the exchanged and unexchanged samples after they were evacuated at 800°C. The argon and krypton isotherms at 25° changed but little when the samples were evacuated at progressively higher temperatures up to 800°C. Likewise there was no major change in the surface areas, though areas after 800° evacuation were about 10% smaller than after evacuation at 450°C.

e. Addition of water vapor back to the sample of unexchanged silica-alumina that had been evacuated at 800° caused the carbon monoxide adsorption at 200 torr and 25°C to return to the same adsorption value it has possessed on being heated to 250°C. Presumably a strong reversible dehydroxylation occured during the 800°C evacuation but reversed itself completely when water vapor was added back at a lower temperature (about 400°C). Possibly the exposure of Si^{+4} and Al^{+3} by evacuating at 800° caused the same type of CO adsorption as caused by exchanged calcium ions. It may be noted that both nitrogen and carbon monoxide possess high quadrupole energies whereas argon and krypton have zero values of quadrupole energies. This may account for the fact that exchanged calcium ions have a large heat of interaction with nitrogen and carbon monoxide but negligible interaction with argon and krypton.

7. Ethylene hydrogenation over cracking catalysts compared to pentene formation by dehydrogenation or cracking of pentane.

The data in the literature are contradictory in regard to the ability of a silica-alumina cracking catalyst to hydrogenate olefins such as ethylene. Some report hydrogenation others deny it. When we recently noted that at small conversions n-pentane formed pentenes as the principal cracking product it became important to know whether the ability of a catalyst to hydrogenate ethylene is related to the ability to form pentenes from pentane.

A comparison was made by Mr. Brenner between the cracking activity at 450°C and the rate of ethylene hydrogenation on catalyst 980 containing 0.03% Fe as impurity, catalyst DS3 made from aluminum propionate and ethyl orthosilicate and a "porous glass" catalyst made by treating well leached Vycor with aluminum nitrate and igniting to form a silica-alumina catalyst. The last two catalysts had negligible amounts of Fe as impurity.

The results showed that the iron free cracking catalysts had very low activities for ethylene hydrogenation but good activities for the dehydrogenation of pentane to pentenes. Furthermore H_2S poisoning showed little effect on the dehydrogenation of pentane to pentene over any of the catalysts but caused the ethylene hydrogenation on catalyst 980 containing 0.03% Fe as impurity to drop its activity to 1/40th of the value on the unpoisoned catalyst. Specifically, the ratio of the ethylene hydrogenating activities was 1:1/20:1/500 on catalyst 980, porous glass and DS3 respectively whereas the ratio of cracking activities for pentane are 1:2/3:1/8 respectively.

The results seem to indicate that at least for isopentane cracking the dehydrogenation to form pentenes is a rapid initial step in catalytic cracking but that ethylene hydrogenation is performed mostly by metallic impurities such as iron in the cracking catalyst.

8. Cracking of low molecular weight hydrocarbons.(19)

Greensfelder and others have explored rather thoroughly the carbonium ion mechanism for cracking hydrocarbons over acidic silica-alumina catalysts. However, his theory automatically restricts itself to hydrocarbons having 7 or more carbon atoms because it involves a postulate to the effect that C_1 or C_2 carbonium ions or gaseous hydrocarbons are not formed during cracking. It seemed worthwhile therefore to study with ^{14}C tracers the decomposition of some of the smaller hydrocarbons such as pentane. This work is all contained in the dissertation of Dr. Robert Garten at the Johns Hopkins University, 1967.(19)

The work can be appropriately covered by the "summary and conclusion" portion of Dr. Garten's dissertation as follows:

"A detailed study of the decomposition of normal pentane and 2-methylbutane over silica-alumina reveals that a description of the kinetics of the decomposition of low molecular weight hydrocarbons as 3/2 order for normal paraffins and 1st order for isoparaffins is an oversimplification. As shown by the work presented here, it is necessary to determine the primary products of the decomposition reaction and to define the influence of these products on rate, kinetics, and kinetic parameters in order to present a more detailed description of the system.

Several important points and conclusions concerning the interaction of normal pentane and 2-methylbutane with silica-alumina catalysts have resulted from this investigation. These are listed below:

(1) The primary products of the decomposition of normal pentane and 2-methylbutane over silica-alumina are very similar differing mainly in the relative amounts formed. In both cases the primary products are mainly olefins.

(2) The pentenes, which occur in thermodynamic equilibrium concentrations, constitute a large fraction of the primary products. The behavior of the pentenes as a function of the time of contact and temperature in a flow system suggests that the primary interaction of the paraffin with the catalyst results in dehydrogenation of the substrate to the corresponding olefin and molecular hydrogen. This dehydrogenation may be sufficient to account for the initiation of paraffin cracking.

(3) Flow system studies as a function of contact time and temperature indicate that the pentenes decompose mainly to C_2- and C_3- fragments (propylene and ethylene). Methane and a large fraction of the butenes, however, do not appear to be formed through the decomposition of the pentenes but apparently result from the decomposition of initially formed C_5- carbonium ions.

(4) The secondary reactions of olefins include skeletal and double bond isomerization, polymerization, and condensation reactions leading to coke formation. The decomposition of surface polymer results in the formation of

paraffin products and is primarily responsible for the formation of these compounds.

(5) n-Pentane forms propane as the major product while 2-methylbutane forms 2-methylpropane as the major product under conditions where olefins can undergo extensive secondary reactions. 2-Methylbutane also tends to form C_6- compounds to a greater extent than does n-pentane. Since the primary product distribution for the two compounds are similar, these results suggest that the polymerization reactions which lead mainly to isoparaffins are partially blocked when n-pentane is the reactant.

(6) Product studies in a circulation system confirmed the results of flow reactor studies in that olefin products underwent extensive secondary reactions leading to the formation of paraffins. Under conditions of olefin removal in a circulation system, large hydrogen production was observed lending support to the dehydrogenation mechanism as the initial step in paraffin cracking.

(7) Olefin removal studies in a circulation system confirmed that olefins are primarily responsible for coke formation and for the formation of paraffins. N-pentane is a better coker than 2-methylbutane. Linear pentenes would result from the direct dehydrogenation of n-pentane, and these compounds may be better coking agents than the branched pentenes which would result from direct dehydrogenation of 2-methylbutane.

(8) Carbon-14 tracer studies of the decomposition of 2-methylbutane-1-C^{14} and 2-methylbutane-4-C^{14} confirmed that polymerization and isomerization resulting in extensive scrambling of carbon-14 occurs in the presence of olefin products in a circulation system. Under conditions of olefin removal the results

lend support to the idea that some direct decomposition of initially formed C_5-carbonium ions occurs prior to skeletal isomerization of the carbonium ions.

(9) Preliminary experiments indicated that the activity of silica-alumina catalysts is affected by the type of oxidation pretreatment used. This is important if kinetic studies are to be performed. Pretreatment of the catalyst in flowing oxygen saturated with water vapor was found to be suitable and give good reproducible catalytic activity.

(10) The olefin products formed when n-pentane or 2-methyl-butane is passed over silica-alumina influence both the kinetics and the kinetic parameters of the decomposition reaction. A summary of the results is shown in Table 41. It is clear from this table that the extent to which olefins are allowed to participate in the reaction affects both the kinetics and the kinetic parameters.

(11) A study of the influence of olefin products on rate in both a circulation system and a flow reactor confirmed that olefins accelerate paraffin decomposition over silica-alumina. The increase in rate can be attributed to the fact that the activation energy for the decomposition reaction in the presence of olefin products, i.e., surface extensively covered with carbonium ions, is less than that observed when olefin products are removed from the reaction system, i.e., catalyst surface relatively bare. The differences in rate in the presence and absence of olefin products do not reflect the observed changes in activation energy due to a compensation effect by the pre-exponential factor.

In the presence of olefins it is concluded that the reactant undergoes activated adsorption on the catalyst primarily by hydride ion transfer to surface

Table 41

A Summary of the Influence of Product Olefins on the Kinetics and Kinetic Parameters of the Decomposition of n-Pentane and 2-Methylbutane Over Silica-Alumina

Product Olefins	Order	Activation Energy (kcal/mole)	Pre-Exponential Factor (molecules/sec/m^2)	Temp.	Parameters used in E_a Determination
			Normal Pentane		
In	3/2	22.3	7.75×10^{16}	400-500°C	3/2 order rate consts.
In	---	19.7	---	400-500°C	Initial rates
Partially removed	3/2	---	---	448°C	---
Completely removed	1/2	32.2	1.10×10^{22}	462-500°C	1/2 order rate consts.
Completely removed	1	39.2	1.06×10^{23}	436-451°C	1st order rate consts.
			2-Methylbutane		
In	2	21.4	2.09×10^{16}	344-450°C	2nd order rate consts.
In	---	19.0	---	344-401°C	Initial rates
In	---	12.1	---	422-451°C	Initial rates
Partially removed	1	20.2	4.24×10^{17}	375-450°C	1st order rate consts.
Completely removed	1/2	32.0	1.11×10^{22}	399-464°C	1/2 order rate consts.
Flow system	---	34.4	---	403-500°C	percent conversion versus temperature

carbonium ions. When olefins are removed, it is probable that a direct interaction between paraffin and catalyst occurs which results in dehydrogenation of the substrate.

(12) The observed influence of olefin products on rate accounts for the presence of an induction period in the catalytic cracking of paraffins under "dry" catalyst conditions."

This then is a summary of the work that has been done with the help of AEC support on catalytic cracking and cracking catalysts. In brief it has given quantitative data as to the extent to which olefins, paraffins and aromatic build-in to form higher molecular weight products during the cracking of cetane over silica-alumina catalysts at 372°C. The olefins are built in extensively, the paraffins very slightly and the aromatics only in a few cases such as involve alkylation with propylene. Coke once formed does not exchange its carbon atoms with hydrocarbons being cracked or with the products of cracking. Aromatics apparently are formed in catalytic cracking by the polymerization or copolymerization of small olefins and not by the cyclodehydrogenation of paraffins.

The addition of 0.1 to 0.2% water to a cracking catalyst increases its cracking activity for hydrocarbons by as much as a factor of 5. The tracer adsorption work for heptane on amorphous silica-alumina suggests that a loosely bound complex or carbonium ion on the catalyst surface is responsible for cracking. The adsorptive characteristics of the surface of a cracking catalyst as judged by the adsorption of nitrogen and carbon monoxide shows that dehydroxylation increases the adsorption of CO and N_2 at 25° and 100 torr by factors of 10 to 20 whereas it does not change the adsorption of either argon or krypton. Restoring the water vapor reduces the adsorption of CO and N_2 to the values characteristic of the original catalyst.

Zeolytic sieve catalysts permit much smaller (1/10th) amounts of radioactive tracer propylene to be built into the hydrocarbons than is characteristic of an amorphous silica-alumina catalyst. The cause of the difference is not known with certainty though presumably it is related to the difficulty of the tracer propylene getting into the 9Å pore opening against the traffic jam caused by the cetane molecules and the decomposition products.

Finally the work has confirmed the fact that ethylene does not tend to form carbonium ions on the surface of cracking catalysts and is therefore not ordinarily formed in appreciable quantities during catalytic cracking of hydrocarbons. Pure silica-alumina catalysts do not hydrogenate ethylene at 350 to 400°C at appreciable rates. As little as 0.03% Fe as impurity will however cause the catalyst to hydrogenate most of the ethylene from a stream of hydrogen-ethylene. The first step in the cracking of pentanes appears to be the formation of a pentyl carbonium ion capable of yielding pentenes as the dehydrogenation product. This dehydrogenation unlike the ethylene hydrogenation is caused by the silica-alumina catalyst itself and not by impurities.

This part of the work is covered by eight publications attached and six dissertations. They will be supplemented by about five papers from the dissertations at the Johns Hopkins University by Robert Garten, 1967 and Burton Bartley, 1966 and John Bardley, 1972.

Iron Catalysts for Ammonia Synthesis and Fischer Tropsch Synthesis Of Hydrocarbons from CO and H_2

Porous promoted iron catalysts have been used in ammonia synthesis for 60 years and in the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen for about 50 years. Because of our continuing interest as a nation in both of these processes we have considered it worthwhile studying the catalysts and both of these processes to obtain a better understanding of the catalytic mechanisms involved and to examine in more detail the characteristics of the iron catalysts that are employed. The results obtained in the three principal groups of experiments will now be summarized.

1. The exchange of $H_2{}^{18}O$ with the oxygen of promoters(12) on the surface of iron catalysts.(12)

For many years it has been known that the addition of 1 to 2% aluminum oxide and a similar amount of potassium oxide would increase the activity and maintain the stability of iron catalysts used for ammonia synthesis. Considerable evidence accumulated to indicate that the few percent of promoter might actually be covering 50% or more of the surface. Actually chemisorption of carbon monoxide and carbon dioxide at -78°C suggested that about 60% of the surface of commercial doubly promoted iron catalysts is covered by promoter after complete reduction of the catalysts and 40% of the surface is iron. When $H_2{}^{18}O$ became available a method for proving the concentration of promoters on the catalyst surface suggested itself. $H_2{}^{18}O$ should exchange its oxygen content with the ^{16}O ions which the promoter molecules contain. Analysis of the $H_2{}^{18}O$-$H_2{}^{16}O$ mixture equilibrated with the iron catalyst at 450° should permit a calculation of the promoter content on the surface provided only that a reasonable size is selected for the oxygen ions of the promoter molecules. The figure selected by Pauling was 10.7Å^2 per oxygen ion. This figure applied to the number of oxygen ions found to be present confirmed the early estimate to the effect that the promoters covered 60% of the catalyst surface. It probably represents the most accurate and reliable figure for promoter distribution on the surface of these iron catalysts which, incidentally are active for both ammonia synthesis from 3:1 H_2:N_2 mixtures and hydrocarbon synthesis from hydrogen-carbon monoxide mixtures.

It should be noted that both Toyoshima and John L. Wishlade spent time on this problem attempting to adopt the small mass spectrograph to the analysis of $H_2{}^{18}O$-$H_2{}^{16}$ mixtures. Their efforts were unsuccessful and will not be reported here. Their efforts were touched on briefly in my report for October, 1962-September, 1963 and from October, 1963 to September, 1964.

2. <u>The inhibition by nitrogen of the chemisorption of carbon monoxide on an unpromoted iron catalyst</u>(13).

Ozaki in Japan has used $^{30}N_2$ tracers to obtain evidence as to whether nitrogen is chemisorbed on ammonia catalysts as molecules or as atoms. His results indicated that on singly or doubly promoted iron catalysts in the 400-450° range no nitrogen molecules could be detected. This agreed with conclusions that we had reached by noting that nitrogen chemisorbed on the iron catalysts at 450° would not inhibit the adsorption of CO on the iron at -195°. This strongly suggested that the nitrogen was present as atoms because the latter are so much smaller than the molecules that they would have a good chance of not interfering with the adsorption of CO. However, Ozaki found that on pure iron catalysts at 380° 80% of the nitrogen appeared to be in the molecular form. Preliminary to planned isotope experiments we have accordingly studied the influence of chemisorbed nitrogen on the chemisorption of CO on pure iron catalysts.

The measurements were made and indicated that at 200°C about 80% of the surface adsorbed nitrogen is on the molecular form. At 300° the percentage drops to about 50% and at 400° to about 25%. The agreement with Ozaki's findings is sufficiently good as to not warrant repeating Ozaki's tracer experiments. Apparently nitrogen adsorption at about 200° can be largely in the molecular form though at 450° on the promoted catalyst it is mostly in the atomic form.

3. The use of C-14 tracers in studying the catalytic Fischer-Tropsch Synthesis of hydrocarbons from carbon monoxide-hydrogen mixtures.(9)(10)

Extensive research over the period 1945 to 1955 showed that the synthesis of hydrocarbons from carbon monoxide-hydrogen mixtures over iron catalysts lead to the conclusion that the mechanism of the reaction involved the formation of oxygen-hydrocarbon complexes on the catalyst surface as intermediates. Specifically, the addition of one percent of radioactive ethyl alcohol to the CO-H_2 synthesis gas passing over an iron catalyst at 250° built in a radioactive content in the hydrocarbons that was approximately constant over the range of carbon numbers extending from C_2 to C_{10}. Furthermore the amount of radioactivity in the products indicated that about one molecule in three of the hydrocarbons came from the radioactive intermediates. In other words the data are consistent with the idea that partially dehydrogenated adsorbed alcohols are intermediates in the synthesis of higher hydrocarbons. Aldehydes and higher alcohols are likewise efficient as intermediates. Olefins such as ethylene and propylene will serve as intermediates though their efficiency is considerably lower than a similar partial pressure of alcohols. Russian work confirmed our results with alcohols and extend the application to as high as C_{32} carbon atoms over cobalt.

All early attempts to find any molecule that would serve as a former of a C_1 intermediate complex were in the early work unsuccessful. Both methanol and formaldehyde were tried but were found to decompose into CO and hydrogen at a rate that was so fast that no starting of a C_1 chain appeared to take place.

In 1956 after the writer had transfered his activities to the Johns Hopkins University he employed Dr. George Blyholder to study ketene, CH_2CO, as an intermediate. In the meantime a new valuable technique in the form of gas liquid partition chromatography had come into use. It therefore became possible to devise a counting apparatus(15) connected directly to a chromatograph in such a way that each of the compounds giving rise to a chromatographic peak would be counted directly in a flow type Geiger counter.

The results obtained by Dr. Blyholder have been published in two papers.(9)(10) In brief he found that the compound CH_2CO (where the asterisk indicates a radioactive carbon) resembled ethyl alcohol in that it formed hydrocarbons with an approximately constant radioactivity per cc over the carbon range C_2 to C_{10}. The amount of radioactivity built in was even larger than that obtained in the earlier work from ethyl alcohol. One conclusion that was tempting to make was that the CH_2CO molecule and the CH_3CH_2OH molecules formed similar intermediate complexes on the iron surface. It became apparent, however, that this could be tested by making experiments with $CH_2\overset{*}{C}O$ as a tracer. If the C_2 complex was being formed then $\overset{*}{C}H_2CO$ and $CH_2\overset{*}{C}O$ would yield the same results. On the other hand, if, as seemed likely, the very reactive ketene molecule was breaking into adsorbed CH_2 groups and gaseous CO then the low molecular weight hydrocarbons would have only a negligible activity and the activity vs. carbon number would be expected to be a straight line extending through the origin.

The experimental results corresponded to the second hypothesis. The low molecular weight hydrocarbons had very small activities. The activity vs. carbon number yielded a straight line passing through the origin. It has a slope of 95 counts per minute per added carbon per cc or hydrocarbon whereas the exit carbon monoxide has an activity of 40 counts per minute per cc of carbon monoxide. Evidently some of the added carbon atoms in building up the higher hydrocarbons come by the direct interaction of ketene molecules with the surface complex though about one-half the slope can be accounted for by the reaction of carbon monoxide from the gas phase. Apparently for the first time these ketene experiments show that adsorbed CH_2 complexes can act as chain initiators.

One factor in the above work lead to some additional as yet unpublished experiments. Ketene is known to be a very unstable molecule. It therefore raises the question as to how ketene could persist through to a bed of iron catalyst at 250°C without decomposing. This prompted us to carry out some more experiments. Dr. Toyoshima constructed an apparatus in which it was possible to sample the gas phase at 5 different points along the catalyst bed. He could determine both the gas composition and the radioactivity of each component. The results of the work can be summed up succinctly by stating that less than 1% of the entering ketene still was present in the gas stream 15% of the distance along the catalyst bed. Accordingly ketene cannot possibly be the component that transfers and carries the radioactive carbon along the length of the reactor.

The next most likely thing that occurred to us that that either ethylene or propylene was the real carrier of the radioactivity through most of the bed. To obtain evidence on this point Dr. Y. Kubokawa carried out some experiments in which he studied both ethylene and propylene as tracers. His results clearly show that both of these gases can act as chain initiators throughout the length of the catalyst bed. However, the efficiency of the chain initiation is only about 1/10th that of the ketene experiments. Hence neither of these can be carrying on for the ketene after the latter disappears near the front end of the catalyst bed. This work too is still being written up for publication. It is clear however that we still do not have an explanation of the ketene experiments in that we do not know which component can be carrying the radioactivity down the catalyst bed and acting as a chain initiator.

In summary we can say that alcohols, olefins, aldehydes and ketene can all function to initiate reaction chains involved in the synthesis of hydrocarbons over iron catalysts from a carbon-monoxide-hydrogen mixture. The mechanism by which ketene operates is still not clear since the added ketene tracer disappears in the first fifteen percent of the catalyst bed.

Equation of State Work

For a number of years Dr. I. Kuhn has been interested in developing an equation of state for various gas-liquid systems. His efforts culminated in publication in 1965 of such as equation as applied to both water and carbon dioxide. The final equation took the form

$$p = \frac{k}{d^3} \left(\frac{\lambda}{d}\right)^{(a/d)^n} T - \frac{f_2}{d^6} + \frac{f_3}{d^4 \lambda^2}$$

where k is the Boltzmann constant, d is the average distance between molecule centers and f_2, f_3, a, n, and d_{min} are adjustable constants. λ is $d-d_{min}$. As can be seen from figure 1 in the attached reprint(22) the equation gives an accurate representation of p-v plots for both water and carbon dioxide when the five constants are fixed by choosing four experimental points on the p-v liquid phase for both systems.

In view of the fact that the Atomic Energy Commission is interested in and has supported work on equations of state, Dr. Kuhn was put on to the general catalytic grant with a supplementary program. His goal was to develop if possible a 3-constant equation for representing the vapor pressure change with temperature for a number of gases. In the attached report(23) work is summarized and discussed for H_2O, CO_2, N_2, Ar, and Ne.

The equation he developed (equation 8 in the attached report of his work) is simply his original 5-constant equation (equation 1) minus the last two terms. This essentially means retaining the kinetic term and dropping the two terms in equation 1 correcting for mutual repulsion and attraction among the molecules. His three-constant equation takes the form

$$p = k\lambda^{(a/d)^n} T \qquad (8)$$

where k is the Boltzmann constant and a, n and d_{min} are adjustable constants, λ being defined as $d-d_{min}$. d is calculated from the $(V_{molal}/N)^{1/3}$, where N is Avogadros number.

In applying his equation to water vapor, carbon dioxide, nitrogen, argon and neon Kuhn makes comparative calculations for a number of other 2- and 3-constant equations that have been proposed as follows:

Kirchhoff	$\log P = A + B/T$	(2-constant)	(2)
Clausius	$\log P = A + B/T + C \log T$	(3-constant)	(3)
Van der Waals	$p = \frac{RT}{v-b} - A/V^2$	(2-constant)	(9)
Berthelot	$p = \frac{RT}{v-b} - A/Tv^2$	(2-constant)	(10)
Redlich-Kwong	$1 = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$	(2-constant)	(11)

A brief evaluation of the relative effectiveness of equation 8 may be made with the help of his calculations in Tables I, II, III and IV taken from his attached manuscript.

Table I (23)

t°C	p_{exp} kg/cm^2	Diff % of p_{calc} related to p_{exp}	t°C	p_{exp} kg/cm^2	Diff % of p_{calc} related to p_{exp}	t°C	p_{exp} kg/cm^2	Diff % of p_{calc} related to p_{exp}
0	0.006228	-0.002	140	3.6848	-0.010	290	75.917	-0.018
5	0.008891	-0.017	150	4.8535	-0.003	300	87.611	-0.021
10	0.012513	-0.021	160	6.3023	0.000	310	100.64	-0.004
20	0.023829	-0.029	170	8.0764	+0.007	320	115.12	+0.025
25	0.032287	-0.030	180	10.225	+0.012	325	122.95	+0.024
30	0.043254	-0.031	190	12.800	+0.022	330	131.18	+0.031
40	0.075204	-0.024	200	15.857	+0.030	340	148.96	+0.051
50	0.12578	-0.015	210	19.456	+0.035	350	168.63	+0.144
60	0.20312	-0.006	220	23.659	+0.037	360	190.42	+0.387
70	0.31775	+0.004	230	28.531	+0.038	365	202.21	+0.605
80	0.48292	+0.011	240	34.140	+0.038	370	214.68	+0.925
90	0.71491	+0.007	250	40.560	+0.028	371	217.26	+0.999
100	1.03323	-0.004	260	47.866	+0.017	372	219.88	+1.057
110	1.4609	-0.012	270	56.137	+0.005	373	222.53	+1.101
120	2.0245	-0.011	275	60.660	0 x	374	225.22	+0.791
130	2.7544	-0.010	280	65.457	-0.007	374.15	225.65	0 x

In the 0-330°C interval the max. diff.% = +0.038, avrg. diff.% = ±0.017
In the 0-crit. interval the max. diff.% = +1.101, avrg. diff.% = ±0.063

Table I -- Results of Equation 8 applied to the saturated water vapor data of Osborne, Stimson and Ginnings (1939). -- x: basic points of calculation.

Table I gives a detailed summary of the effectiveness of equation 8 as applied to the vapor pressure of liquid water from 0°C to the critical temperature 374.15. The percentage deviation from the experimental data is truly remarkably small. Between 0° and 340° the deflations are only a few hundredths of a percent. Between 350 and the critical temperature they range from 0.1% to 1.1%.

Table II(23)

t°C	p_{exp} kg/cm^2	Eq. 2	Eq. 9	Eq. 10	Eq. 11	Eq. 3	Eq. 8
		DIFFERENCE % = 100 (p_{calc}/p_{exp} −1)					
0	0.006228	0 x	+0.044	+0.035	+0.040	0 x	-0.002
50	0.12578	-17.749	+0.257	+0.166	+0.216	-10.259	-0.015
100	1.03323	-21.674	+0.847	+0.459	+0.657	-11.502	-0.004
150	4.8535	-19.781	+1.714	+0.775	+1.212	- 8.961	-0.003
220	23.659	-13.095	+2.462	+0.966	+1.525	- 3.557	+0.037
275	60.660	-6.998	0 x	0 x	0 x	0 x	0 x
325	122.95	-2.228	-12.743	-5.191	-5.913	+ 1.531	+0.024
370	214.68	+0.038	-93.994	-45.425	-31.047	+ 0.367	+0.925
374.15	225.65	0 x	0 x	0 x	0 x	0 x	0 x
Max. diff.%		-21.674	-93.994	-45.425	-31.047	-11.502	+0.925
Avrg. diff.%		± 9.062	±12.451	± 5.891	±4.512	± 4.020	±0.112

Table II -- Two theoretically derived equations, three simple equations of state, and Eq. 8 applied to some states of saturated water vapor. x: basic points of calculation.

Table II affords a comparison among the various equations of state as applied to water vapor. It is evident that for water vapor equation 8 is in a class by itself.

Table III$^{(23)}$

t°K	p_{exp} int. atm.	Eq. 2	Eq. 9	Eq. 10	Eq. 11	Eq. 3	Eq. 8
		DIFFERENCE % = $100(p_{calc}/p_{exp}-1)$					
trp. 83.78	0.679						
120.327	12.197	0 x	0 x	0 x	0 x	0 x	0 x
126.047	16.478	+0.796	-0.991	+1.624	+0.075	-0.291	+0.038
130.110	20.108	+1.173	-2.021	+1.283	+0.029	-0.305	-0.004
134.981	25.166	+1.446	-3.981	+2.229	+0.052	-0.171	-0.071
139.163	30.190	+1.471	-6.574	+3.251	+0.104	0 x	-0.123
142.803	35.135	+1.296	-10.022	+4.270	+0.163	+0.128	-0.131
146.135	40.175	+0.959	-14.935	+5.136	+0.170	+0.198	-0.076
148.186	43.554	+0.635	-19.412	+5.335	+0.083	+0.179	+0.060
149.660	46.132	+0.324	-23.324	+4.730	-0.158	+0.112	+0.209
150.475	47.622	+0.108	-23.438	+2.904	-0.438	+0.039	+0.617
crit. 150.86	48.34	0 x	0 x	0 x	0 x	0 x	0 x
Max. diff.%		+1.471	-23.438	+5.335	-0.438	-0.305	+0.617
Avrg. diff.%		±0.746	± 9.509	±2.524	±0.116	±0.144	±0.125

Table III--The six equations of Table II applied to some states of the saturated vapor for argon. x: basic points of calculation.

Table III gives a comparison among the various equations for the data on argon from its triple point at 83.78°K up to its critical temperature, 150.86°K. Surprisingly, equations 3, 11 and 8 all give about equally good representations of the experimental data.

Table IV(23)

	t°C	p_{exp} int. atm.	Eq. 11	Eq. 3	Eq. 8
			Diff. % =	100 (p_{calc}/p_{exp}-1)	
		Nitrogen			
trp.	-210.01	0.124			
	-205.45	0.2673	-0.541	0 x	-0.269
	-195.09	1.0875	-1.129	-3.648	-0.481
	-182.51	3.767	-0.992	-2.880	+0.042
	-161.20	16.335	0 x	0 x	0 x
	-153.65	24.13	+2.741	+1.685	+0.432
	-148.61	30.90	+3.737	+1.486	-0.146
crit.	-147.19	33.49	0 x	0 x	0 x
	Maximum:		+3.737	-3.648	-0.481
	Average:		±1.306	±1.386	±0.196
		Carbon dioxide			
trp.	-56.25	5.110			
	-50	6.746	+1.382	0 x	+0.558
	-30	14.082	+0.795	-0.718	+0.229
	-15	22.589	0 x	-0.457	0 x
	0	34.397	-1.032	0 x	-0.187
	+15	50.260	-2.527	+0.345	-0.070
	+20	56.580	-3.461	+0.426	-0.102
	+25	63.481	-4.150	+0.461	+0.739
crit.	+31	72.549	0 x	0 x	0 x
	Maximum:		-4.150	-0.718	+0.739
	Average:		±1.668	±0.301	±0.244
		Neon			
trp.	-248.59	0.42763			
	-240.00	4.4630	0 x	0 x	0 x
	-239.34	5.0901	-0.334	-0.098	-0.426
	-237.04	7.7746	+1.652	-0.134	+1.224
	-235.50	10.060	+2.638	0 x	+1.788
	-232.125	16.957	+3.860	+0.271	+1.150
	-230.80	20.058	+3.415	+0.276	-0.517
	-230.07	22.098	+3.469	+0.229	-1.273
crit.	-228.75	26.193	0 x	0 x	0 x
	Maximum:		+3.860	+0.276	+1.788
	Average:		±1.921	±0.126	±0.797

Table IV-- Equations 11, 3, and 8 applied to some states of the saturated vapor for nitrogen, carbon dioxide, and neon. x: basic points of calculation.

Table IV contains the comparison of equations 3, 11 and 8 on nitrogen, carbon dioxide and neon. For nitrogen equation 8 is clearly superior to either equations 11 or 3. For carbon dioxide it is about the same as equation 3 but clearly superior to 11. For neon it is superior to 11 but clearly inferior to equation 3.

Thus, in summary, Dr. Kuhn has constructed a simplified 3-constant equation which represents pressure vs temperature data in a remarkably precise manner. The work suggests that for still other gases one might expect favorable results. Unfortunately Dr. Kuhn died January 6, 1973 so this brief account of his work is based on his manuscript (attached) without any final consultation with him.

Miscellaneous Projects

A number of miscellaneous projects were worked on. Some of them were completed and published. Most of them were incomplete. A few will still be published. The following includes a brief summary of the final status and conclusions from these projects.

1. Equilibrium measurements in the Molybdenum-Carbon-Hydrogen System.(14)

The equilibrium for the reaction

$$2Mo + CH_4 = Mo_2C + 2H_2 \qquad (1)$$

was studied by Browning and myself on samples of Mo_2C formed by carbiding the Mo with carbon monoxide. A few years ago Gleiser and Chipman pointed out that the data of Browning and Emmett lead to an impossibly high (26 entropy units) entropy change for the reaction

$$2Mo + C = Mo_2C \qquad (2)$$

In view of these facts we decided to redetermine the equilibrium constants for reaction 1.

The most obvious source of error in the measurements made by Browning and Emmett was the possible contamination of the Mo_2C with molybdenum oxide during the carbiding with carbon monoxide. Such contamination could result in CO, CO_2 and H_2O being present at a steady state in addition to methane. Unfortunately in the work of Browning and Emmett a thermal conductivity analysis method was used so that all such gaseous impurities would be mistaken for methane with the resulting production of an abnormally low equilibrium constant for reaction 1. Accordingly, it was decided to avoid this source of error by preparing the Mo_2C by carbiding molybdenum with methane under such pressures as to avoid the formation of free carbon and also with the complete absence of any contamination due to oxygen.

Equilibrium data lead to a standard free energy change for reaction 1 given by the equation

$$\Delta F^\circ = 8410 - 26.44\ T$$

For reaction 2 the free energy change was given by the equation

$$\Delta F^\circ = 12{,}030 - 1.44\ T$$

The entropy change for reaction 2 is thus small and in agreement with the value estimated from the work of Gleiser and Chipman. Furthermore the data for reaction 2 plot up on a free energy-temperature plot to show good consistency with the plot of the data of Gleiser and Chipman taken at a somewhat higher temperature range.

The elimination of any effects due to impurities such as water vapor, CO_2 or CO was assured by continually circulating the equilibrating H_2-CH_4 mixture through a liquid nitrogen trap. This removed the water vapor and carbon dioxide directly and the CO indirectly by permitting it to react with the Mo with the resulting formation and removal of CO_2.

The data are discussed and presented in detail in the enclosed reprint. It should be pointed out that these data were determined on the project with the help of a specific AEC appropriation because of the importance of knowing the exact value of the equilibrium in reaction 1 because of possible occurence of this reaction in the molten salt reactor and in other nuclear systems.

2. The Gas Chromatographic Determination of Hydrogen, Deuterium and HD.(11)

An aluminum oxide chromatographic column operating at -195°C was shown to be capable of analyzing hydrogen for its ortho- para ratio, using helium as a carrying gas. An equilibrated H_2-D_2 mixture yielded three peaks. One was for ortho and para deuterium (unresolved); a second was for HD and ortho hydrogen and a third for para hydrogen. Finally by using hydrogen as a carrying gas deuterium and HD could be determined. A combination of these runs permitted one to obtain values for ortho-hydrogen, para-hydrogen HD and deuterium. Agreement between the HD and H_2 and D_2 in an equilibrated mixture is good for HD values higher than about 10%.

3. The exchange of radioactive acetone with isopropyl alcohol and propylene during the catalytic dehydrogenation and dehydration of isopropyl alcohol over chromium oxide catalysts.

Dr. G. Kremeric switched from NSF support to AEC support for three months to explore the use of radioactive tracers in helping to understand some of the puzzling results that he had been finding for isopropyl alcohol dehydrogenation to acetone and hydrogen and dehydration to propylene and water over chromium oxide catalysts. He had observed that above 350°C the dehydrogenation reaction to acetone had a negative temperature coefficient whereas below that temperature the temperature coefficient was positive. Radioactive acetone was added to the original isopropyl alcohol in a series of experiments covering the temperature range 300 to 450°C. He found that over this entire range some of the radioactivity of the acetone was transfered back to the isopropyl alcohol despite the fact that the equilibrium constant for the dehydrogenation to acetone and hydrogen was in the range 100 to 1000. Some radioactivity was also found in propylene but this is to be expected since the propylene is formed by the dehydration of the isopropanol. Also some of the radioactive acetone might be formed by direct hydrogenation of the acetone.

Dr. Kreminic did not have time to do more than a preliminary survey of the use of tracers in this reaction. The results were too incomplete to warrant publication.

4. The chromatographic analysis of nitric oxides.

In response to the needs in some of the AEC laboratories for an easy method for analyzing gas mixtures for NO and NO_2 some preliminary gas chromatographic work was undertaken by Mr. Matsushita. All attempts to separate NO and NO_2 by chromatographic analysis had been unsuccessful. Preliminary results obtained by him in the few months he worked on the problem indicates that a chromatographic column filled with "porous glass" (the product obtained during the manufacture of Vycor) offers good possibilities. The column must first be carefully baked out at about 750°C to free it from water vapor and most of the surface -OH groups.

NO emerges from the column with a short retention time at 25°. NO_2 on the other hand emerges only above 150°C. Even at this high temperature a certain amount of chemisorption appears to take place. In some of the last experiments it was found that the chemisorption of the NO_2 could be largely eliminated by preliminary acid leaching of the porous glass to remove sodium ions. It looked as though a successful separation of NO and NO_2 on a leached and baked column may be practicable. Unfortunately time did not permit bringing this work to a publishable stage.

In conclusion the work of Bruce Bell should be mentioned. During one summer he set up an apparatus for studying the polymerization of propylene to hexenes and the copolymerization of propylene and isobutene to form heptenes. Unfortunately the work had to discontinued before any results were obtained. When the writer left the Johns Hopkins University in July 1970 Bruce Bell transfered his work to Dr. R. J. Kokes. He continued to work on a problem that I had assigned him, namely a study of the oxidation by free oxygen of ammonia adsorbed on cracking catalysts to form free nitrogen. The original work had been done and published by Dr. Skala of the Univeal Oil Products Corp. We planned to reexamine her very puzzling results and hoped by using tracers to explain some of her observations. Unfortunately the work had to be discontinued after a few months because of a breakdown suffered by Mr. Bell that forced him to withdraw from the University.

He made a few preliminary runs that seemed to confirm Dr. Skala's main contention that chemisorbed ammonia on silica-alumina cracking catalyst can be oxidized in the 300 to 500°C temperature range with the formation of free nitrogen.

The present report covers work done in the Chemistry Department at The Johns Hopkins University from July, 1957, to July, 1971. It includes experiments performed by Dr. George Blyholder, John Bordley, Allan Brenner, Bruce Bell, Burton Bartley, Robert Garten, Joe Hightower, Dr. Yun-yang Huang, Dr. George Keulks, Dr. G. Kreminic, Dr. Esteban Kuhn, Dr. Yutaka Kubokawa, Kun-ichi Matsushita, Dr. Age Solbakken, Wilfred Solbakken, Willian Van Hook, Dr. John L. Wishlade, and Dr. I. Toyoshima. Nine were postdoctorates and nine were students. It has included work for six dissertations, fifteen publications besides thesis dissertations, and an estimated seven additional papers that are in various stages of preparation and should be published over the next several years.

The assistance of the Atomic Energy Commission in financing all of this work is hereby greatfully acknowledged.

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