SPECIAL REPORT OF RESEARCH

Conducted in

Department of Fuel Technology
College of Mineral Industries
The Pennsylvania State University

THE ISOTHERMAL KINETICS
OF
VOLATILE MATTER RELEASE
FROM ANTHRACITE

by

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and
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STATEMENT OF TRANSMITTAL

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SR-12  Removal of Mineral Matter from Anthracite by Chlorination at High Temperatures  June 22, 1959

SR-13  Radiation Stability of a Coal Tar Pitch  June 25, 1959

SR-14  The Effect of Nuclear Reactor Irradiation During Low Temperature Carbonization of Bituminous Coals  July 31, 1959

SR-15  Effect of Anthracite and Gamma Radiation at Ambient Temperatures on the Subsequent Plasticity of Bituminous Coals  August 5, 1959

M. E. Bell, Director
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SUMMATION OF RESULTS

The isothermal kinetics of hydrogen evolution from St. Nicholas anthracite were studied and found to be such as would be expected for the desorption of a gas which is chemisorbed on to the surface. The rate of hydrogen release appears to follow a zero order law during the initial stages of the reaction, where the surface coverage is greater than 95%. When the surface coverage falls below 95%, however, a gradual deviation from zero kinetics was observed, and in this range the volume of hydrogen evolved was found to be proportional to the logarithm of the time. The energy of activation for the desorption of hydrogen from anthracite was determined for various surface coverages and was found to vary linearly with the fraction of surface covered. The energy of activation for zero coverage was found by extrapolation to be approximately 180 kcals. per mole.

The effect of particle size on the rate of hydrogen desorption was studied, and it was found that for St. Nicholas anthracite the rate of hydrogen release increases with increasing particle size. This, however, was not found to be the case for other anthracites. The rate of volatile matter evolution from Loree anthracite was observed to decrease with increasing particle size, while from Dorrance and Glen Burn anthracites the rate of desorption decreases to a minimum with increasing particle size and was then found to increase. For Jeddo anthracite a slight maximum in the rate of desorption was observed with increasing particle size.

It is thought that the effect of particle size on the rate of volatile matter release bears some relationship to the decrepitation properties of an anthracite.
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ABSTRACT

The kinetics of hydrogen release from St. Nicholas anthracite were investigated isothermally, and a desorption mechanism postulated. The results obtained indicate that hydrogen is chemisorbed on to the anthracite surface.

Volatile matter release rates were determined for various anthracites and the effect of particle size observed. The variation of volatile release rates with particle size was found to depend markedly upon the nature of the anthracite.
INTRODUCTION

The fact that anthracite has a tendency to decrepitate when subjected to appreciable temperature gradients, is a serious disadvantage to its use as a metallurgical fuel (1). Since it would be of economic advantage to employ anthracite in metallurgical processes, a considerable amount of work has been carried out at the Pennsylvania State University with a view to increasing the thermal stability of selected anthracites.

It is thought that the release of volatile matter during the primary thermal decomposition is an important factor in the decrepitation of anthracite, and attempts have been made to decrease the rate of this release by controlled preheat-treatment. In this way, it should be possible to reduce the intra-particle pressure build-up to below that value which will cause physical disintegration of the coal structure.

In order to avoid the obvious disadvantages of trial and error methods for ascertaining the conditions for successful preheat-treatment, an attempt was made by E. T. Nelson (1) to deduce the most significant variables involved and the manner in which they are related mathematically. During the course of this work, which involved studies of volatile matter release at linear heating rates, it was found desirable to know something about the kinetics of volatile release under isothermal conditions.

If the decrepitation of anthracite is primarily concerned with the considerable evolution of volatile matter which occurs upon heating, then in order to understand the mechanism whereby this takes place it is essential to investigate the process isothermally. It has been shown (1) that the major constituent of the volatiles evolved above 700°C. is...
hydrogen; and, therefore, it would seem feasible to concentrate attention primarily upon the production of this gas.

A study of the relationship between the volume of hydrogen evolved isothermally and time should provide valuable information as to the type of reaction which is taking place. The temperature dependence of the velocity constant can be even more illuminating, since perhaps the most important parameter in reaction kinetics is the energy of activation. Such data should enable a fairly accurate estimation to be made of the rate processes involved in the formation and evolution of hydrogen from anthracite; whether they be chemical in nature - such as the decomposition of compounds or surface complexes formed by chemisorption, or physical - such that mass or heat transfer are of primary importance.

It may be that decrepitation is caused by a combination of effects - only one of which is volatile matter release. Nevertheless, it is of great importance to determine the mechanics of the most elementary processes, otherwise it is unlikely that an overall understanding can be attained. On the other hand, if the release of volatiles is the primary cause of structural disintegration, it is quite possible that a careful study of the kinetics of gas evolution could, in conjunction with other work proceeding in this laboratory, not only provide a solution for the mechanism of decrepitation but also a means of prevention.

ACKNOWLEDGMENT

The authors wish to thank E. T. Nelson for his assistance in
the early stages of this work, and also R. Anderson who carried out the volatile matter analyses.

OBJECTIVES

The main objective in a study of the isothermal kinetics of gaseous evolution from anthracite is the elucidation of the mechanism whereby such coals decrepitate.

In metallurgical processes the fuel is subjected to non-isothermal conditions, and investigations of practical value have already been made into volatile matter release from anthracite at linear heating rates (1). These studies do not, however, lead to a satisfactory determination of the fundamental mechanism of volatile release. It is desirable, therefore, to carry out further investigations isothermally in order to determine the type of reaction (or reactions) which is occurring and, if possible, to evaluate the most important parameters involved. Once these are known, it is probable that the process of decrepitation will be more fully understood.

EXPERIMENTAL PROCEDURE

The measurement of rates of hydrogen release from anthracite was carried out in an apparatus similar to that described by E. T. Nelson (1). This consisted of a 1 KW, 20 volts Hoskins tube furnace and transformer, the power input to which was controlled by means of a Leeds and Northrup Speedomax H temperature control unit capable of maintaining a preset temperature within 2°C. The furnace temperature was measured by a chromel-alumel thermocouple which was protected by a ceramic tube and was recorded by the control unit.
The furnace was connected to a Beckman gas chromatography unit, which was equipped for the analysis of hydrogen content with a 6 foot column of Linde 13X Molecular Sieves used in conjunction with argon as a carrier gas. The electrical output from the thermal conductivity detector cell was fed to a Minneapolis-Honeywell 1 millivolt range recorder, which traced a curve showing the separation of the sample into its components.

The volume of total volatiles evolved was found by displacement of water from a 5 liter aspirator at constant pressure.

Each experiment was carried out in the following way: A known weight of anthracite (about 5 grams) was placed in a quartz tube, which in turn was contained within a Coors Sillimanite furnace tube of 1 inch internal diameter. The thermocouple was then placed inside the quartz tube, and in close contact with the sample; after which, the whole apparatus was flushed with nitrogen to provide an inert atmosphere. With the nitrogen supply cut off and the system open only to a water manometer, the furnace was switched on; the preset temperature (varying between 700 and 850°C.) being reached within 15 to 20 minutes. The volatiles evolved passed through a water-cooled condenser into the gas chromatography unit, where samples from an inlet valve were analyzed at time intervals of 5 or 10 minutes. The total volume of volatiles was measured by means of an aspirator (maintained at atmospheric pressure). From a calibration curve of percentage composition of hydrogen against trace peak height, the volume of hydrogen evolved at standard temperature and pressure was easily calculated.
This procedure was followed in all the work to be described, except where otherwise specified.

**EXPERIMENTAL RESULTS**

Preliminary Experiments - Preliminary experiments were carried out on St. Nicholas anthracite of particle size 150 x 200 mesh to determine whether any simple relationship exists between the volume of hydrogen evolved and the time of reaction; and if so, whether reproducible results could be obtained. St. Nicholas anthracite was chosen in the first instance because this was used by E. T. Nelson for evolution studies at linear heating rates, and some correlation between the two series of investigations was hoped for.

An arbitrary fixed furnace temperature (above 700°C.) was chosen and the volume of hydrogen evolved during ten minute intervals determined. A plot of the cumulative volume of hydrogen released against time was found to be approximately linear between average limits of about 5 and 30 mls. of hydrogen evolved. It would appear, therefore, that initially the reaction is of zero order, i.e. dq/dt is a constant, where q is the volume of hydrogen evolved and t is the time. Several such experiments were performed, and in all cases the values obtained for dq/dt for the same sample weight and furnace temperature were reproducible within the limits of experimental error.

In order to determine the rate constants in terms of concentration, it was necessary to know the exact volume of gas in the apparatus at atmospheric pressure. The level of water initially in the aspirator was marked and the volume $V_0$ occupied by gas to this point determined,
by perfect gas law calculations, to be 1502 mls. In subsequent experiments, the aspirator was initially filled to the same mark and the concentration of hydrogen present in the apparatus at any given time calculated as follows: If \( v' \) is the volume of hydrogen evolved in liters and \( V \) the total volume of volatile matter evolved, the molar concentration of hydrogen is \( \frac{v'}{22.4 \times \frac{1}{(V_0 + V)}} \) moles liter\(^{-1}\).

It is not strictly necessary to express the rate constants in terms of moles liter\(^{-1}\) sec.\(^{-1}\); and since it is somewhat tedious to do so, later results are given in mls./min.

**Determination of an Activation Energy** - The initial rates of hydrogen release from St. Nicholas anthracite (150 x 200 mesh) were determined at temperatures ranging from 700 to 755°C. The results obtained from a typical run are shown in Table 1 and the plot of hydrogen evolved against time in Figure 1. It was found that above 760°C., the reaction proceeded at too great a rate to enable an accurate measurement of the zero order velocity constant to be made; this will be discussed in detail later.

In the zero order range, the rate of reaction is equal to the velocity constant \( k \), and since \( k = Ae^{-E/RT} \) (Arrhenius) - it should be possible to calculate the energy of activation \( E \). The plots of hydrogen concentration against time obtained at varying temperatures are shown in Figure 2, and Table 2 is a record of the corresponding values determined for \( k \). It was found that the plot of \( \log k \) against \( 1/T \) is linear (Fig. 3), and from the slope the energy of activation was calculated to be 96 Kcals./mole. This value for \( E \) is high and, hence, shows that the
TABLE 1

HYDROGEN RELEASE FROM ST. NICHOLAS ANTHRACITE

Furnace Temperature = 710°C.  Weight of Sample = 5.54 grams.

<table>
<thead>
<tr>
<th>Time in Mins.</th>
<th>Average Percentage H₂*</th>
<th>Vol. of Volatiles at S.T.P. in mls. †</th>
<th>Vol. of H₂ at S.T.P. in mls.</th>
<th>Conc. of H₂ in moles/liter x 10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>initial - 62.85</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.50</td>
<td>25.66</td>
<td>0.13</td>
<td>0.36</td>
</tr>
<tr>
<td>20</td>
<td>2.25</td>
<td>18.59</td>
<td>0.42</td>
<td>1.53</td>
</tr>
<tr>
<td>30</td>
<td>5.35</td>
<td>9.04</td>
<td>0.48</td>
<td>2.84</td>
</tr>
<tr>
<td>40</td>
<td>9.10</td>
<td>9.04</td>
<td>0.82</td>
<td>5.08</td>
</tr>
<tr>
<td>50</td>
<td>12.80</td>
<td>8.85</td>
<td>1.13</td>
<td>8.13</td>
</tr>
<tr>
<td>60</td>
<td>16.30</td>
<td>7.97</td>
<td>1.30</td>
<td>11.62</td>
</tr>
<tr>
<td>70</td>
<td>18.60</td>
<td>7.08</td>
<td>1.32</td>
<td>15.15</td>
</tr>
<tr>
<td>80</td>
<td>19.60</td>
<td>5.31</td>
<td>1.06</td>
<td>17.96</td>
</tr>
<tr>
<td>90</td>
<td>21.00</td>
<td>5.31</td>
<td>1.12</td>
<td>20.90</td>
</tr>
<tr>
<td>100</td>
<td>20.60</td>
<td>7.08</td>
<td>1.46</td>
<td>24.72</td>
</tr>
</tbody>
</table>

Rate Constant k = 5.48 x 10⁻⁸ moles liter⁻¹ sec⁻¹

* Average percentage of hydrogen evolved during ten minute periods.

† Volume of volatile matter evolved during ten minute periods.
710° C

TIME IN MINUTES
ZERO ORDER PLOT
OF HYDROGEN CONCENTRATION AGAINST TIME FOR 150 × 200 MESH ST. NICHOLAS ANTHRACITE

Figure 1
THE VARIATION OF INITIAL HYDROGEN RELEASE RATES WITH TEMPERATURE FOR 150 × 200 MESH ST. NICHOLAS ANTHRACITE

Figure 2
reaction under consideration is almost certainly chemical in nature.

A Proposed Mechanism for the Production of Hydrogen from Anthracite —

As the furnace temperature was increased — so the evolution of hydrogen became more rapid, until a point was reached when it was found impossible to measure the zero order rate constant accurately — so short was the duration of linearity. At 800°C., no linear relationship between the concentration of hydrogen and the time was observed; but it was found that a plot of the volume (or concentration) of hydrogen evolved against the logarithm of time gave a perfectly straight line after only a few minutes. This behavior is identical to that observed for the release of hydrogen from graphite (2) and is to be expected for the desorption of gases which are chemisorbed on a heterogeneous surface.

In order to determine whether or not the hydrogen evolved from anthracite was previously chemisorbed to the surface, it becomes necessary to review the theory of chemisorption and desorption (3):

---

**TABLE 2**

RATE CONSTANTS FOR THE INITIAL RELEASE OF HYDROGEN FROM ST. NICHOLAS ANTHRACITE

<table>
<thead>
<tr>
<th>Furnace Temperature in °C.</th>
<th>700</th>
<th>710</th>
<th>720</th>
<th>725</th>
<th>740</th>
<th>750</th>
<th>755</th>
</tr>
</thead>
<tbody>
<tr>
<td>k in moles liter⁻¹ sec⁻¹ x 10⁸</td>
<td>3.60</td>
<td>5.48</td>
<td>7.91</td>
<td>13.32</td>
<td>21.99</td>
<td>36.55</td>
<td>48.61</td>
</tr>
</tbody>
</table>
DETERMINATION OF AN ACTIVATION ENERGY FOR
THE DESORPTION OF HYDROGEN FROM
150 × 200 MESH ST. NICHOLAS ANTHRACITE
(θ ≈ 1)

Figure 3
Adsorption may occur whenever gas molecules possessing the necessary activation energy $E$ collide with surface sites available for chemisorption. The chance that such collisions result in adsorption is known as the condensation coefficient $\sigma$. The velocity of adsorption depends on:

1. the rate of collisions with the surface - this is, on unit area and pressure $p$: $p/\sqrt{2\pi m kT}$, where $m =$ mass of a gas molecule,
2. the magnitudes of $\sigma$ and $E$, and
3. the chance that collisions take place at available sites. Since this is usually dependent upon the fraction of surface coverage, $\theta$, it is designated $f(\theta)$.

The velocity of adsorption (chemisorption) is then:

$$u = \frac{\sigma P}{\sqrt{2 \pi mkT}} \cdot f(\theta) \cdot e^{-E/RT} \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

The velocity of desorption depends upon:

1. the number of sites, $f'(\theta)$, from which desorption is possible,
2. the activation energy of desorption $E'$, and
3. a velocity constant $K$.

The velocity of desorption is then:

$$u' = K \cdot f'(\theta) \cdot e^{-E'/RT} \cdot \cdot \cdot \cdot \cdot \cdot (2)$$

where $E'$ is equal to the sum of the activation energy and the heat of adsorption, $E$ and $Q$.

Certain modifications to equations 1 and 2 are required if $E$, $E'$, $K$, and $\sigma$ vary with $\theta$. There are two reasons for this:
(1) Variations may arise from repulsive interactions in a layer - these depend on interatomic distance and hence upon \( \theta \). In this case the surface may be treated as uniform, that is in adsorption into a layer of given \( \theta \), all available sites will have the same \( E \) and \( \sigma \) values; and in desorption \( K \) and \( E' \) will be the same at all available sites.

The velocities are obtained by inserting in equations 1 and 2 the functional dependence of \( E, E', K \) and \( \sigma \) upon \( \theta \):

\[
u' = K(\theta) \cdot f'(\theta) \cdot e^{-E'(\theta)/RT} \]

\[
u'' = K(\theta) \cdot f''(\theta) \cdot e^{-E'(\theta)/RT} \]

(2) A more frequent cause of variation of \( E, E', K \) and \( \sigma \) is that surfaces are heterogeneous, i.e. there is a variation of adsorptive property from site to site, with different sites possessing different values of these four quantities. Dividing the total surface area into a number of small uniform elements \( dx \), each containing \( n_x \) sites of type \( x \), and to each of which equations 1 and 2 apply:

\[
u = \frac{p}{\sqrt{(2 \pi mkT)}} \int n_x \sigma_x f(\theta_x) e^{-E_x/RT} dx \]

\[
u'' = \int n_x K_x f'(\theta_x) e^{-E'_x/RT} dx \]

In deriving the velocity of desorption, statistical equilibrium is assumed between adsorbed molecules and activated complexes. The latter vibrate perpendicular to the surface with a frequency \( v \), which is the frequency of decomposition of the complexes. In this equilibrium, surface sites play no part - and the equilibrium constant is given by

\[k^* = c^*/c_a = f^*/f_a\]

where \( f^* \) and \( f_a \) are the complete partition functions of the complexes.
and the adsorbed molecules respectively, and the c's are their concentrations. Separating the zero point energies from the partition functions; and from f* the term \( kT/h \) due to the vibration perpendicular to the surface, we have:

\[
c*/c_a = kT/h \cdot f*/f_a \cdot e^{-E'/RT}
\]

The velocity is then:

\[
u' = v \cdot c* = c_a \cdot kT/h \cdot f*/f_a \cdot e^{-E'/RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (6)
\]

If the fraction of sites available for desorption is \( f'(\varnothing) \), and the total number is \( n_s \) per cm.\(^2\), then \( c_a = n_s \cdot f'(\varnothing) \). Inserting this in equation 6 and comparing the resulting equation with that for desorption from a uniform surface, \( u' = K \cdot f'(\varnothing) \cdot e^{-E'/RT} \), we have:

\[
K = n_s \cdot kT/h \cdot f*/f_a \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (7)
\]

If the complexes and adsorbed molecules possess identical degrees of freedom, \( f* \) is equal to \( f_a \) and

\[
K = n_s \cdot kT/h \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (8)
\]

Equation 7 does not hold if association takes place during desorption. If \( 2\, RS \rightarrow R_2S_2* \rightarrow R_2 + S_2 \), then the velocity of desorption becomes:

\[
u' = kT/h \cdot c_a^2 \cdot f*/f_a^2 \cdot e^{-E'/RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (9)
\]

Therefore,

\[
K = n_s \cdot kT/h \cdot f*/f_a^2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (10)
\]

If the complexes and adsorbed radicals are both immobile, \( f* = f_a = 1 \), therefore, \( K = n_s \cdot kT/h \). If both radicals and complexes are mobile,
that is desorption of hydrogen chemisorbed on a metal surface as atoms, the two translational degrees of freedom are lost in forming the complex, therefore, tending to make \( f^*/f_a^2 \) less than unity. However, this will to some extent be offset by the rotational partition function being appreciable for the complex but unity for the adsorbed atoms.

Part of the variation of velocities with \( \theta \) is located in the terms \( f(\theta) \) and \( f'(\theta) \) of equations 1 and 2. These terms represent the fractional numbers of sites available for adsorption and desorption respectively. They arise because adsorption often takes place only through collision of a gas molecule with an uncovered site, and desorption is only possible from covered sites. As a result, \( f(\theta) \) tends to be largest at low \( \theta \) and \( f'(\theta) \) largest at high \( \theta \).

The variation of velocity with \( \theta \) is only solely located in terms on \( f(\theta) \) and \( f'(\theta) \), if the quantities \( E, E', K \) and \( \sigma \) are independent of \( \theta \). In adsorption, \( \sigma \) probably approaches unity at all \( \theta \) values, and if in addition adsorption is non-activated this condition is obeyed. However, if adsorption is activated, \( E \) seems to increase with \( \theta \), and the main variation of velocity with \( \theta \) may be due to this. In desorption, \( E' \) and also \( K \) are probably always dependent on \( \theta \), and the main variation of velocity is more likely to be located in these than in the term \( f'(\theta) \).

When the coverage is \( \theta \), the fractional number of uncovered single sites is \((1 - \theta)\). The chances that a colliding molecule strikes a vacant site for mobile and immobile layers alike is \( f(\theta) = 1 - \theta \). Similarly, desorption can proceed from any single occupied site, and
hence \( f'(\theta) = \theta \). However, if a molecule (such as hydrogen) dissociates to give two radicals each of which occupies one site, then for mobile layers it can be shown that

\[
u' = K_1 \theta^2 e^{-E'/RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (11)\]

With non-activated adsorptions, the variation of velocity with \( \theta \) resides solely in statistical terms. In activated adsorptions, and in all desorptions, there is evidence that the activation energies \( E \) and \( E' \) respectively increase and decrease as \( \theta \) increases, and the dependence of velocity upon \( \theta \) may arise primarily from this. In particular, if \( E \) and \( E' \) vary linearly with \( \theta \), according to equations

\[
E = E_0 + \alpha \theta \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12)
\]

and

\[
E' = E_0' - \beta \theta \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (13)
\]

for which there is experimental evidence, velocity equations may be derived which prove to be quite widely obeyed.

There are two possible reasons why \( E \) and \( E' \) should vary with \( \theta \). If the surface is homogeneous, the variation is due to surface interactions; if it is heterogeneous, it is due to sites possessing different adsorptive properties. In both cases adsorption on a single site will be considered:

(1) A Uniform Surface: Since all sites are identical, it is possible to substitute in the velocity equations

\[
u = \frac{\sigma p}{\sqrt{2 \pi m k T}} \cdot (1 - \theta) \cdot e^{-E/RT}
\]

and
\[ u' = K \theta \cdot e^{-E'/RT} \]

the values of \( E \) and \( E' \) from equations 12 and 13. Assuming that \( \sigma \) and \( K \) do not vary greatly with \( \theta \), this gives

\[ u \propto (1 - \Theta) \cdot e^{-\alpha \theta /RT} \]

and

\[ u' \propto \theta \cdot e^{\beta \theta /RT} \]

Provided in adsorption \( \Theta \) is not close to unity, we may neglect the variation of \( (1 - \Theta) \) in comparison with the variation in \( e^{-\alpha \theta /RT} \). Similarly in desorption, except when \( \Theta \longrightarrow 0 \), the term \( e^{\beta \theta /RT} \) is more important. Under such conditions,

\[ u \propto e^{-\alpha \theta /RT} \] \hspace{1cm} (14)

\[ u' \propto e^{\beta \theta /RT} \] \hspace{1cm} (15)

(2) A Non-Uniform Surface. It can be shown (4) that in this case, equations 14 and 15 also hold.

The velocity equations are therefore:

\[ d\Theta/dt = a \cdot e^{-\alpha \theta /RT} \] \hspace{1cm} (16)

and

\[ -d\Theta/dt = b \cdot e^{\beta \theta /RT} \] \hspace{1cm} (17)

and on integration these give respectively:

\[ \Theta = RT / \alpha \cdot \ln \left( t - t_o \right) / t_o \] \hspace{1cm} (18)

where \( t_o = RT / \alpha a \)

and

\[ \Theta = RT / \beta \cdot \ln \left( t'_o / t \right) \] \hspace{1cm} (19)
where \( t'_0 = \frac{RT}{\beta b} \)

Although \( \sigma \) may often be independent of \( \Theta \), \( K \) may vary considerably as a layer fills. At present there are too few figures available to formulate this effect with any certainty.

It has been found that the evolution of hydrogen from anthracite at 800°C. follows the kinetic scheme given by equation 17, and since energies of activation for desorption are often very high (5), it seems more than likely that hydrogen is present on anthracite in the chemisorbed state.

The initial zero order evolution can be explained simply by assuming that for raw anthracite the fraction of surface covered, \( \Theta \), is practically unity. If almost all the sites available for hydrogen adsorption are filled, then equation 11 reduces to \( u' = A.e^{-E'/RT} \), where \( A \) is a constant. This is identical with the equation for a zero order reaction; and the energy of activation, 96 Kcals./mole, is therefore that for complete surface coverage. It was found that approximately 600 mls. of hydrogen could be desorbed from 5 grams of St. Nicholas anthracite, and about 30 mls. were evolved according to a zero order law. If \( \Theta \) is assumed to be initially 1, and 600 mls. of adsorbed hydrogen are taken to constitute complete surface coverage, then \( \Theta \) will be reduced from 1 to 0.95 by the desorption of 30 mls. of gas. It is quite conceivable that such a small percentage change in \( \Theta \) will not affect the rate of reaction. In order to check whether or not this hypothesis is correct, it is desirable to determine the activation energies for other values of \( \Theta \).
If these, together with the activation energy for complete surface coverage, vary linearly with \( \theta \) (according to equation 13), then it is probable that the postulated mechanism for hydrogen evolution from anthracite is correct.

The following method was devised for determining activation energies for varying values of \( \theta \): From equation 11, the rate of desorption is given by

\[
-dq/dt = K \cdot \theta^2 \cdot e^{-E'/RT}
\]

where \( q \) is the volume of hydrogen evolved. Also, from equation 8, \( K = T \), therefore

\[
-dq/dt = a \cdot T \cdot \theta^2 \cdot e^{-E'/RT}
\]

where 'a' is a constant. If the rate of desorption is found at different temperatures for the same surface coverage (i.e. equal values of \( q \)), then from an Arrhenius plot of \( \log(dq/dt \cdot 1/T) \) against \( 1/T \) it should be possible to calculate \( E' \) for that value of \( \theta \). \( dq/dt \) can be found as follows: Since \( dq/d\log t \) is constant, \( dq/dt = \text{constant}/t \), where \( t \) is the time when \( q \) mls. of hydrogen have been evolved. \( \theta \) is then \( 1 - q/x \) where \( x \) is the total volume of hydrogen initially present on the surface.

The plots of volume of hydrogen evolved against log time are shown in Figure 4, and the values obtained for \( \log(dq/dt \cdot 1/T) \) at various temperatures and values of \( \theta \) are listed in Table 3. It was necessary to know the exact values for \( t \) corresponding to selected volumes of evolved hydrogen, \( q \). Experimentally, \( t \) was taken to be zero when the required furnace temperature \( T \) was reached; however, a finite time elapsed before \( T \) was attained - and also an estimated volume of gas was evolved. Errors were, therefore, involved in the values for \( t \) read from the \( q/\log t \) plots. Correc-
THE VARIATION OF $dq/d \log t$ WITH INCREASING TEMPERATURE FOR 150 x 200 MESH ST. NICHOLAS ANTHRACITE

Figure 4
TABLE 3
VARIATION OF LOG (dq/dt·1/T) WITH θ AND T

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>5 + log(dq/dt·1/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>2.1314</td>
</tr>
<tr>
<td>810</td>
<td>2.5282</td>
</tr>
<tr>
<td>825</td>
<td>2.8326</td>
</tr>
<tr>
<td>850</td>
<td>3.3139</td>
</tr>
<tr>
<td>860</td>
<td>3.8780</td>
</tr>
<tr>
<td>800</td>
<td>1.5614</td>
</tr>
<tr>
<td>810</td>
<td>2.0382</td>
</tr>
<tr>
<td>825</td>
<td>2.3626</td>
</tr>
<tr>
<td>850</td>
<td>2.8739</td>
</tr>
<tr>
<td>860</td>
<td>3.4280</td>
</tr>
<tr>
<td>800</td>
<td>0.9814</td>
</tr>
<tr>
<td>810</td>
<td>1.4582</td>
</tr>
<tr>
<td>825</td>
<td>1.8026</td>
</tr>
<tr>
<td>850</td>
<td>2.3533</td>
</tr>
<tr>
<td>860</td>
<td>2.8880</td>
</tr>
<tr>
<td>800</td>
<td>0.3114</td>
</tr>
<tr>
<td>810</td>
<td>0.9782</td>
</tr>
<tr>
<td>825</td>
<td>1.3326</td>
</tr>
<tr>
<td>850</td>
<td>1.9239</td>
</tr>
<tr>
<td>860</td>
<td>2.4480</td>
</tr>
</tbody>
</table>

| 810               | 0.3082            |
| 825               | 0.6826            |
| 850               | 1.3139            |
| 860               | 1.8280            |
tions were made by plotting \( q \) against \( t \) and taking tangents at particular values of \( q \) in order to find \( dq/dt \). Logt at \( q \) can therefore be found, and the original logt axis corrected.

Activation energies for \( \theta = 0.88, 0.80, 0.70, 0.62 \) and 0.50 were calculated to be 107, 112, 122, 128 and 137 Kcals./mole respectively (Fig. 5). The plot of activation energy against \( \theta \) (from 1 to 0.50) was found to be linear (Fig. 6); and on extrapolation to zero coverage, a value of approximately 180 Kcals./mole was found for \( E^0 \).

It would seem, from the results given above, that hydrogen is in fact desorbed from the surface of anthracite - and that this is the rate determining step. It is possible, however, that the process is not so simple as it would at first appear - and it is desirable to carry out further experiments with different particle sizes and anthracites, in order to determine whether the proposed mechanism is able to explain all the observed facts.

**The Effect of Particle Size on the Rate of Desorption of Hydrogen from St. Nicholas Anthracite** - The rate of evolution of hydrogen from St. Nicholas anthracite of particle size 12 x 16 mesh was found to be greater than from the same weight of a smaller particle size (150 x 200 mesh). Table 4 shows values obtained for the rate constants of the initial zero order reaction at various temperatures, and compares them with those obtained from anthracite of 150 x 200 mesh size. From these results, it was possible to calculate an activation energy of about 89 Kcals./mole for the initial desorption of hydrogen from St. Nicholas anthracite of mesh size 12 x 16 (Fig. 7).
DETERMINATION OF ACTIVATION ENERGIES
FOR VARYING VALUES OF $\theta$
FOR 150 x 200 MESH ST. NICHOLAS ANTHRACITE

Figure 5
THE VARIATION OF ACTIVATION ENERGY WITH θ FOR 150 × 200 MESH ST. NICHOLAS ANTHRACITE

Figure 6
TABLE 4

THE EFFECT OF PARTICLE SIZE ON THE RATE CONSTANT FOR HYDROGEN RELEASE FROM ST. NICHOLAS ANTHRACITE

<table>
<thead>
<tr>
<th>Particle Size (Tyler Mesh)</th>
<th>Temperature in °C.</th>
<th>Rate Constant k in mls./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 x 16</td>
<td>700</td>
<td>0.17</td>
</tr>
<tr>
<td>150 x 200</td>
<td>700</td>
<td>0.08</td>
</tr>
<tr>
<td>12 x 16</td>
<td>710</td>
<td>0.27</td>
</tr>
<tr>
<td>150 x 200</td>
<td>710</td>
<td>0.13</td>
</tr>
<tr>
<td>12 x 16</td>
<td>725</td>
<td>0.41</td>
</tr>
<tr>
<td>150 x 200</td>
<td>725</td>
<td>0.30</td>
</tr>
<tr>
<td>12 x 16</td>
<td>730</td>
<td>0.68</td>
</tr>
<tr>
<td>12 x 16</td>
<td>740</td>
<td>1.00</td>
</tr>
<tr>
<td>150 x 200</td>
<td>740</td>
<td>0.50</td>
</tr>
<tr>
<td>12 x 16</td>
<td>750</td>
<td>1.50</td>
</tr>
<tr>
<td>150 x 200</td>
<td>750</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Figure 8 shows the plots obtained for the volume of hydrogen evolved from anthracite of varying particle size against time; and it is seen that the larger the particles - the greater the rate of evolution. The rate of hydrogen release from consolidated anthracite is considerably greater than from the same weight of a -325 mesh sample. Whatever the particle size, however, the volume of gas evolved against time curves are of an identical form in all cases, being initially linear and gradually changing to logarithmic. This would seem to indicate that the same mechanism for release is operating for all particle sizes. Such
DETERMINATION OF THE ACTIVATION ENERGY FOR DESORPTION OF HYDROGEN FROM 12 × 16 MESH ST. NICHOLAS ANTHRACITE

Figure 7
VARIATION OF THE INITIAL RATE OF HYDROGEN RELEASE WITH PARTICLE SIZE FOR 5.5 GRAMS OF ST. NICHOLAS ANTHRACITE

Figure 8
behavior, however, is difficult to explain on the basis of a chemical desorption as the rate determining process, and the problem will be discussed fully in Section IV.

The Effect of Sample Weight on the Rate of Desorption of Hydrogen from St. Nicholas Anthracite - Experiments were carried out with varying weights of St. Nicholas anthracite and the results found to be somewhat anomalous. It would be expected that the rate of evolution of hydrogen at constant temperature should vary linearly with the sample weight and that such a plot should pass through the origin. The results (listed in Table 5) indicate a linear relationship between the rate of hydrogen release from anthracite of particle size 150 x 200 mesh and the sample weight, where the latter is greater than 3.5 grams. These linear plots determined at temperatures of 750 and 740°C do not, however, pass through the origin. For St. Nicholas anthracite 12 x 16 mesh, there appears to be no linearity.

There is no theoretical significance to these results, so that it seems probable that the method is at fault. The rates of hydrogen release were determined by measuring the volume of volatile matter evolved in a certain period of time and finding the percentage of this which is hydrogen by means of gas chromatography. A close inspection of the data shows that after a given time, the percentage of hydrogen in the evolved gas decreases with the sample weight. If, however, the total volume of gas evolved during a given time is plotted against the sample weight - a straight line plot is obtained, which passes through the origin. It is quite impossible to explain a change in per-
TABLE 5  
THE EFFECT OF SAMPLE WEIGHT ON RELEASE RATES OF HYDROGEN FROM ST. NICHOLAS ANTHRACITE

<table>
<thead>
<tr>
<th>Particle Size (Tyler Mesh)</th>
<th>Temperature in °C.</th>
<th>Sample Weight in grams</th>
<th>Rate of Hydrogen Evolution in mls./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 x 200</td>
<td>740</td>
<td>2.9</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.5</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.9</td>
<td>1.70</td>
</tr>
<tr>
<td>150 x 200</td>
<td>750</td>
<td>4.0</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.5</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.4</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.9</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>2.00</td>
</tr>
<tr>
<td>12 x 16</td>
<td>750</td>
<td>2.1</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.5</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>4.17</td>
</tr>
</tbody>
</table>

The percentage hydrogen with sample weight, and it is obvious that this effect is caused by an error in the method.

If the evolved gases are diluted to some extent by the purge gas nitrogen - which in fact they are - the apparent percentage of hydrogen will be less than the true value. Only when all the nitrogen has been swept from the furnace and column can the chromatograms be regarded.
as giving valid results. It was thought that this error was negligible, but this is evidently not the case for low sample weights and, therefore, low rates of volatile matter release. If the percentages of hydrogen at given times are taken to be those observed with a sample weight of 10 grams (i.e. greatest volume of volatile matter evolved and therefore more chance of all the nitrogen being displaced), then it is found that the volume of hydrogen evolved after, say 25 mins., is directly proportional to the weight of the sample (Table 6 and Fig. 9).

**Volatile Matter Evolution from Loree, Dorrance, Glen Burn, and Jeddo Anthracites** – A number of experiments were carried out using anthracites other than St. Nicholas, in order to determine whether or not the kinetics for gas evolution were similar for a range of coals.

It was found that the percentage of hydrogen was high, and remained fairly constant in the range where dq/dlog t is equal to a constant. The rates of evolution of total volatile matter were, therefore, measured, since the kinetic scheme was essentially the same as for hydrogen release.

(i) **Loree Raw Coal**: It was found that dq/dlog t at 800°C. for Loree anthracite decreased with increasing particle size. The results obtained for the larger sized particles were rather inconsistent, but the trend was quite definite.

(ii) **Dorrance Anthracite**: In this case, dq/dlog t decreased with increasing particle size to a minimum and then increased.

(iii) **Glen Burn Anthracite**: Glen Burn anthracite was found to
TABLE 6
THE VOLUME OF HYDROGEN EVOLVED FROM VARIOUS WEIGHTS OF ST. NICHOLAS ANTHRACITE

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>20.5</td>
</tr>
<tr>
<td>6.4</td>
<td>32.2</td>
</tr>
<tr>
<td>8.0</td>
<td>36.6</td>
</tr>
<tr>
<td>10.0</td>
<td>46.7</td>
</tr>
</tbody>
</table>

Furnace Temperature = 750°C.  
Particle Size (Tyler Mesh) = 150 x 200

behave in a similar manner to Dorrance anthracite, dq/dlog increasing initially with increasing particle size, and then increasing.

(iv) Jeddo Anthracite: The rate of volatile matter release from Jeddo anthracite was found to increase to a slight maximum with increasing particle size, after which the rate decreases markedly.

The results obtained for the five anthracites studied are summarized in Table 7, which also lists the volatile matter content as percentage by weight.

DISCUSSION

Desorption of Hydrogen from St. Nicholas Anthracite - From the isothermal kinetics of hydrogen release from St. Nicholas anthracite,
THE RELATIONSHIP BETWEEN
VOLUME OF HYDROGEN DESORBED
AND
SAMPLE WEIGHT FOR 150 × 200 MESH
ST. NICHOLAS ANTHRACITE

Figure 9
TABLE 7

RATES OF VOLATILE MATTER RELEASE FROM A SELECTION OF ANTHRACITES

Furnace Temperature = 800°C. Sample Weight = approximately 5.5 grams.

<table>
<thead>
<tr>
<th>Anthracite</th>
<th>Volatile Matter Content (percentage by weight)</th>
<th>Particle Size (Tyler Mesh)</th>
<th>dq/dlog t</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Nicholas</td>
<td>4.5</td>
<td>-325 150 x 200 12 x 16</td>
<td>142.0 160.0 183.0</td>
</tr>
<tr>
<td>Loree</td>
<td>5.4</td>
<td>-325 150 x 200 16 x 20</td>
<td>217.0 191.0 176.5</td>
</tr>
<tr>
<td>Dorrance</td>
<td>4.9</td>
<td>-325 150 x 200 12 x 16</td>
<td>153.0  83.0  191.5</td>
</tr>
<tr>
<td>Glen Burn</td>
<td>6.1</td>
<td>-325 150 x 200 16 x 20</td>
<td>158.6 123.0 190.0</td>
</tr>
<tr>
<td>Jeddo</td>
<td>2.9</td>
<td>-325 150 x 200 16 x 20</td>
<td>166.6 170.0 131.8</td>
</tr>
</tbody>
</table>

there seems to overwhelming evidence for the desorption of chemisorbed hydrogen being the rate determining step. There is, however, difficulty in correlating the observed increase in rate of desorption upon increas-
ing the particle size with this theory - although a possible explanation for this phenomenon can be tentatively put forward as follows:

If the rate of desorption of hydrogen from anthracite is given by the expression:

\[ u' = K \cdot T \cdot \theta^2 \cdot e^{-E' / RT} \]  

(where \( u' \) is the rate of desorption, \( K \) is a constant, \( T \) is the temperature, \( \theta \) is the fraction of surface covered, and \( E' \) is the energy of activation for desorption), it is evident that an increase in the rate of desorption can be caused by either (a) an increase in surface coverage, or (b) an increase in temperature.

(a) Unless a considerable quantity of hydrogen is lost by anthracite during the grinding process, thereby reducing the value of \( \theta \) for smaller particle sizes, it is difficult to see how the surface coverage could be higher the larger the particle size. Since there is no apparent evidence for any evolution of gases during grinding, it is unlikely that there is an appreciable change in \( \theta \) for varying particle sizes.

(b) A more probable cause of the change in rate of evolution of hydrogen with particle size is that of temperature variation. If the thermal conductivity of anthracite is partially dependent upon the particle size, then it is possible that the center of the anthracite sample is at a lower temperature (as recorded by the regulating thermocouple) than the outside - this difference in temperature being more pronounced for the larger particle sizes. There is little evidence that this would in fact be the case, indeed there will be more gases in the voids between the smaller particles which will tend to make them poorer conductors of
heat; however, there is some doubt as to the effect of particle size on conductivity (6).

In order to test whether there is a temperature gradient through the anthracite samples, two series of experiments were performed. The first was designed to detect any change in the rates of volatile matter release with position of the regulating thermocouple, and Fig. 10 shows plots of volatile matter evolved against time for samples of St. Nicholas anthracite of particle sizes 150 x 200 mesh and 12 x 16 mesh, with the thermocouple placed first inside the sample (a), and secondly just outside the sample (b);

viz. (a)  (b)

In the latter case the rate was found to be considerably decreased, but this could be due to the fact that the positioning in the furnace was changed - as also was the form of the containing vessel used (in experiments (b), the anthracite was placed in an open boat for convenience). These results were regarded as inconclusive, and further experiments were carried out using a second thermocouple (II) placed parallel to the controller (I); that is

Thermocouple II was connected to a calibrated potentiometer, and the temperature recorded by this was compared with that on the Speedomax control unit. Numerous experiments were carried out for different particle sizes and at varying temperatures, and in all cases there was no detectable difference between the temperatures as given by the
VARIATION OF RELEASE RATES WITH POSITION OF REGULATING THERMOCOUPLE FOR 5.5 GRAMS OF ST. NICHOLAS ANTHRACITE

Figure 10
thermocouples I and II. It was concluded, therefore, that there is no appreciable temperature gradient across the anthracite samples. If then, the change in rate of desorption with particle size is caused by a temperature effect, this must occur within the particles themselves. A tentative theory explaining how this may come about will be described as follows:

The processes involved in the desorption of hydrogen from anthracite are thought to be:

1. Desorption of atomic hydrogen from the surface, involving the breaking of carbon-hydrogen bonds:

\[ 2 \text{C-H} \rightarrow 2 \text{C} + 2 \text{H}. \]

The energy required to break a carbon-hydrogen bond can be taken to be approximately 92 Kcals./mole, although there are some authorities who believe that the dissociation energy for hydrogen chemisorbed to carbon is considerably less than this value.

2. \[ 2\text{H} \rightarrow \text{H}_2 \]

The combination of two atoms to form the hydrogen molecule would release about 103 Kcals./mole.

The total energy required for reactions (1) and (2) will, therefore, be:

\[- (2 \times 92) + 103 = -81 \text{ Kcals./mole}.\]

If the formation of a carbon-carbon bond is also involved, then the required energy will be:

\[- (2 \times 92) + 103 + 39 = -42 \text{ Kcals./mole}.\]

This is equal and opposite to the heat of chemisorption, \( Q \).
Considering the above potential energy diagram, it would be supposed that the process of desorption follows the curve BA, that is to say that the energy change is the exact opposite from that of adsorption AB. This would necessarily involve the formation of a transition complex of the type $C_2H_2^*$, i.e. the process of desorption would be:

$$2\text{C-H} \rightleftharpoons C_2H_2^* \rightleftharpoons 2\text{C} + \text{H}_2.$$ 

However, this is not necessarily the only mechanism for desorption - since the hydrogen can also be desorbed in the atomic form. This subject is fully dealt with in "The Adsorption of Gases on Solids" by A. R. Miller (7), who considers the desorption of hydrogen from tungsten. The complications involved when anthracite is the adsorbent will be outlined later.

When a tungsten filament is heated to a sufficiently high temperature in hydrogen, there is a considerable production of atomic hydrogen.
Since dissociation of the hydrogen molecule occurs upon adsorption, there are several possible processes at the surface to be considered:

(1) (a) Evaporation of atoms from the adsorbed film. (b) An atom from the gas strikes the surface where there is a vacant site and condenses.

(2) (a) Two neighboring adsorbed atoms combine and evaporate as a molecule. (b) A molecule strikes the surface where two neighboring sites are vacant, dissociates and the atoms are adsorbed.

(3) (a) A gas atom strikes an adsorbed atom, combines with it and the two evaporate as a molecule. (b) A gas molecule strikes the surface where there is one vacant site or more, one atom is adsorbed, the other goes into the gas phase.

It can be shown that for low surface coverages, atomic hydrogen is mainly produced by the process (1) (a), and for high surface coverages by (3) (b).

It can also be shown from energy considerations that there is a distinct difference between the true heat of adsorption $Q$, and the apparent heat of adsorption as calculated from the rate of evaporation - even presupposing that the important process in desorption is the combination of adsorbed atoms and the subsequent evaporation of molecules. It is quite probable, therefore, that the desorption of hydrogen does in part consist of evaporation of atoms prior to recombination. This could particularly be the case where the adsorbed atoms are distant from one another, since the energy needed to bring them into adjacent sites may
conceivably be greater than that required to desorb the adsorbate as atoms instead of molecules.

When considering anthracite as the adsorbent, the problem is further complicated by the fact that the internal surface is far greater than the external surface and is comprised of capillaries of molecular dimensions. This being the case, the mobility of the adsorbed species will very probably be hindered to some extent — hence increasing the probability of desorption of atomic hydrogen. A further complication is introduced by the presence of other adsorbates than hydrogen.

Desorption of atomic hydrogen in addition to molecular hydrogen from anthracite suggests a possible explanation for the observed increase in rate of evaporation of H₂ from anthracite of increasing particle size. When atomic hydrogen is desorbed, it will combine to form hydrogen molecules with the evolution of 103 Kcals. of energy per mole. However, this combination will occur at a finite rate (8, 9, 10). Since it is also a third order reaction — collision with either another H atom or with H₂ is required. This means that it is probable that the atomic hydrogen will diffuse a certain distance before combination can occur. In this case, there will be a certain number of H atoms which will escape from the anthracite particles. The percentage of these will be greater the smaller the particle size, and hence the energy lost to the surface will be greater the smaller the particles. It is evident, therefore, that although the exterior of the anthracite is kept at a constant temperature by means of the regulating thermocouple, the interior surface could be at a higher temperature for larger than for smaller particles.
In other words, the apparent activation energy of desorption will be lower for the larger particle sizes.

Desorption of Volatile Matter from Loree, Dorrance, Glen Burn, and Jeddo Anthracites - It has been found that all anthracites do not desorb gases in a manner completely analogous to St. Nicholas anthracite. Kinetically, the release of volatile matter appears to be the same in all cases - but the variations in the rates of release with particle size show quite different trends depending upon which anthracite is considered. This is not surprising in view of the complex nature of anthracites and the manner in which they were formed. The conditions under which gases were initially adsorbed or complexed on to the basic carbon structure would no doubt vary immensely with location - and it is to be expected that the desorptive properties of different coals will be dissimilar. Indeed, it may be that even samples of the same coal will show some variation in behavior - although this would not be expected to be so pronounced as that observed between anthracites from different origins.

It has been shown that the rate of desorption of volatile matter from St. Nicholas anthracite increases with particle size and that for Loree raw coal this tendency is reversed. Dorrance and Glen Burn anthracites apparently behave in yet another manner, the rate of desorption first decreasing to a minimum with increasing particle size and then increasing. The rate of volatile release from Jeddo anthracite is found to exhibit a slight maximum with increasing particle size. A possible explanation for the increase in rate of desorption with increasing particle size has already been put forward - it remains still
another effort, therefore, to suggest a reason for the reversal of this effect.

A decrease in volatile matter release rate with increasing particle size would at first seem to indicate that diffusion is the rate determining step. In fact it has been found that for metals, both activated diffusion and activated adsorption or desorption show similar properties (11). Indeed there has been considerable argument as to whether reversible chemical adsorption may not be activated diffusion, and vice versa. If diffusion is rate determining in the case of gas release from anthracite, then the rate of this release would be expected to decrease with increasing particle size. The reversal of this effect could be attributed to the formation of macro-cracks in the structure caused by pressure build-up, and a consequent increase in release rate. There are several disadvantages to this theory however; the activation energies involved are far greater than would be expected for activated diffusion, and also the observed kinetic scheme is typical for desorption rather than diffusion (which is usually of the first order, i.e. \( \frac{d \log q}{dt} = \text{constant} \)).

If then desorption is rate determining, there must be complications involved which probably arise from the occurrence of processes such as those listed in section A.

Desorption is important when the temperature in degrees Kelvin divided by the heat of adsorption is greater than 20. Now in the case of anthracite, the temperature of desorption is around 1000°K to 1100°K, and the heat of adsorption will be approximately 50 Kcals./mole. This
means that desorption will occur to a greater extent than adsorption. However, there will almost certainly be some re-adsorption, since the evolved gases are not evacuated from the system — which is maintained at atmospheric pressure.

If re-adsorption of hydrogen molecules with dissociation occurs, then the rate of adsorption will be:

\[ \sigma \frac{P}{\sqrt{2\pi mkT}} \cdot (1 - \varnothing)^2 \cdot e^{-E/RT} \]

adsorption must be activated in view of the large energies involved. In addition to the re-adsorption of molecules, there will also be sorption of hydrogen atoms as such — and of one atom from a molecule while the other remains in the gas phase. However, these processes will not be so important as the re-adsorption of molecules, and the overall rate of gas evolution can be written:

\[ \text{Rate of Hydrogen Release} = \frac{K \cdot \varnothing \cdot e^{-E'/RT}}{A} - \frac{\sigma P}{\sqrt{2\pi mkT}} \cdot (1 - \varnothing)^2 \cdot e^{-E/RT} \]

It can be seen that as \( \varnothing \) decreases, \( B \) will increase.

It is evident that the larger the particle size, the more chance there is of re-adsorption within the molecular sieve structure of the anthracite, and therefore the overall rate of hydrogen release should decrease with increasing particle size. However, adsorption is an exothermic process and this together with the combination of hydrogen atoms will tend to increase the temperature of the internal surface. Thus it is possible for re-adsorption to decrease the overall rate of hydrogen release with increasing particle size, up to a point when the surface temperature becomes great enough to reverse this effect.
A Correlation between Volatile Matter Release and Decrepitation - If the decrepitation of anthracite is mainly due to volatile content, it would be expected that the greater the percentage of volatiles present the greater will be the chance of decrepitation occurring. Some justification for this supposition has been found, since in many cases an anthracite with a low volatile matter content will decrepitate less readily than one with a higher volatile content. This is by no means the only criterion for ease of structural disintegration, however, and it is evident that there must be other factors involved.

It is possible that the variation in rate of evolution of volatile matter with particle size is an indication of the decrepitation properties of an anthracite. The plots of $dq/d\log t$ against particle size (Fig. 11) show that there is a gradual change in shape of the curve for the five anthracites which have been studied. It is seen that the curves change in stages from those exhibiting a maximum to those showing a distinct minimum. This can be attributed to a combination of effects such as those indicated in previous sections.

If an increase in rate of volatile evolution is attributed to an increase in the internal temperature of the particles, it is possible that this together with the rapid cooling which will result from an increase in gaseous release, will contribute to the structural weakening of the anthracite. This will arise mainly from differential expansion - which will almost certainly occur.

If, on the other hand, diffusion is more important than has been supposed - it is possible that a rapid increase in rate of gaseous evolu-
QUALITATIVE VARIATION OF \( \frac{dq}{d \log t} \) WITH PARTICLE SIZE FOR VARIOUS ANTHRACITES

Figure 11
tion with increasing particle size is caused by the formation of macro-cracks in the structure of the anthracite. It is likely that, once formed, these cracks will become large enough to weaken the structure sufficiently to eventually cause decrepitation.

It is difficult to prove unequivocally which of these theories, if either, is correct. However, it seems reasonable to assume that the observed effects do have some bearing on the theory of decrepitation. It is also evident that such effects - determined isothermally - will be enhanced when the anthracites are subjected to considerable temperature gradients (although their occurrence under non-isothermal conditions will no doubt be difficult to observe experimentally).

**CONCLUSIONS**

It can be concluded from the observed results that decrepitation will be more likely to occur in anthracites which exhibit a marked and sudden increase in rate of volatile evolution above a certain particle size. Thus, it may be postulated that Dorrance and Glen Burn anthracites will decrepitate more easily than Jeddo and St. Nicholas; Loree anthracite probably occupying an intermediate position - as indicated in Figure 11.
LIST OF REFERENCES


4. Ibid., pp. 104.

5. Ibid., pp. 81.


