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THE KINETICS OF COAL OXIDATION

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ABSTRACT

Seven coals from across Canada were oxidized, and a kinetic analysis made from the data obtained. It was established that the equation[1],

$$\frac{-\mathrm{d}P_i}{\mathrm{d}t} = \frac{K_s\left[P_i\frac{B_1}{B_w} + B_1\,\mathrm{w} - B_1\right]\cdot(B_w W)^{0.50}}{(B_w - P_i)^{0.50}} = K_s'' P_i/(B_w - P_i)^{0.50}$$

is a valid rate of sorption of oxygen in the temperature range 110 to 170°C.

INTRODUCTION

A kinetic equation was developed[1] and used to calculate the rate of oxygen sorbed in the oxidation of two coals.

In order to establish the validity of this kinetic equation, the work was extended to the study of the oxidation of representative Canadian coals from across Canada.

Jones[2] applied the kinetic equation to four coals of different rank from across Canada with some success. The object of this study is to apply it to the same coals which Jones used (but at different temperatures of oxidation), and to extend it to some more coals from other parts of Canada in order to test the applicability and reproducibility.

EXPERIMENTAL

Apparatus

Schematic diagrams of the oxidation apparatus and oxidation bulb are shown in Figs. 1 and 2.

Procedure

Preparation of samples. Samples to be analyzed were prepared from seven different ranks of coal from across Canada. They were ground to 106 μm particle size, and dried in a vacuum oven at 40°C for 28 h.

Description of apparatus. An accurately known weight of approximately 5 g was introduced into the oxidation bulb. A calibrated 360°C thermometer was placed in the bulb and held in place by a stainless steel mesh and two nichrome wires. Seven grams of crushed potassium hydroxide pellets were held in place in the neck of the bulb with glass wool (Fig. 2).

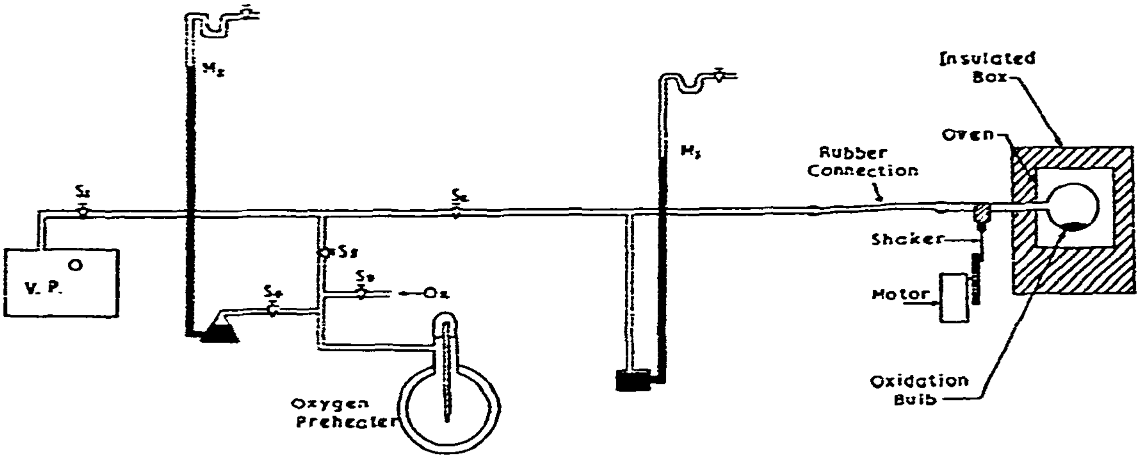

Fig. 1. Oxidation apparatus.

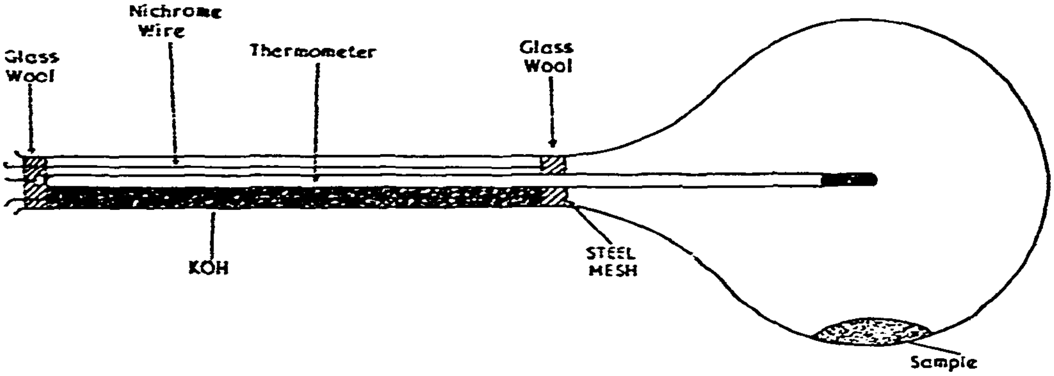

Fig. 2. Oxidation bulb.

The bulb was then placed in an accurately thermostated electric oven with its neck protruding through one of the two circular holes. Through the other hole another 360°C thermometer was affixed so that the mercury bulb was directly above the one in the reaction flask. The neck of the flask was fastened to a geared shaker electric motor. This arrangement caused the coal particles to undergo a 'tumbling' motion making available new surfaces for oxygen–coal contact. The mouth of this reaction bulb was connected to a mercury manometer, M_1 (Fig. 1).

This assembly was connected to the oxygen source–oxygen preheater (thermostatically controlled), manometer, M_2, and a vacuum pump. This is a constant volume system.

Standard procedure. With stopcock, S_3, closed, the shaker was started and the system evacuated to about 10 mm Hg pressure. With S_2 closed, the rest of the system was pumped out for an additional 10 min; S_1 was closed and oxygen admitted to the oxygen preheater through S_3 to a pressure of 760 mm. S_3 was then closed, S_1 opened and the systems exhausted and refilled with oxygen. S_5 was then closed and the system from the vacuum pump to S_2 was evacuated. S_2 was opened, the oven was turned on to the correct temperature and the system pumped out for 8 h. S_1 and S_4 were now closed and the preheater turned on and left on overnight.

Oxygen at the reaction temperature was admitted to the reaction flask at that temperature to a pressure of 760 mm Hg on M_1. The time at which $P_i = 760$ mm was recorded as zero time. The pressure was recorded at 5 to 30 min intervals.

Data

The data obtained for the oxidation of these samples are similar, and therefore a representative table (Table 1) is sufficient to give an idea of how these data were noted. Also, due to the length of the run(s) only some readings will be listed.

Tables 2–8 give additional data on the reactions: the weight of coal used; the initial pressure as obtained from graphs (Figs. 3–10); the weight of oxygen sorbed in the process; $K_s^{0.60}$ as calculated by a method which will be discussed; and K_s.

Throughout these tables the symbol, △, was used to represent Jones' results; and ○ for the author's.

RESULTS AND DISCUSSIONS

The kinetic analysis

Data obtained[1] from successive oxidation of a coal sample showed that there was a retardation which was proportional to the square root of the amount of oxygen consumed. Assuming that the rate is directly proportional to the oxygen pressure, they arrived at the rate equation for a first order reaction for w g of coal as:

$$\frac{-\mathrm{d}P_i}{\mathrm{d}t} = \frac{K_s'' P_i}{(B_w - P_i)^{0.50}} \tag{1}$$

Where: P_i = oxygen pressure at any time, t

K_s'' = rate constant

$B_w = P_0 + b_w$ = the calculated "effective initial pressure".

P_0 cannot be measured accurately since a rapid sorption takes place during the short time required for the addition of oxygen to the system. b_w = the difference in pressure required to make the coal sample used, equivalent to a fresh coal which had not undergone any appreciable oxidation; i.e., it is a pressure correction factor.

TABLE 1

DATA FOR THE OXIDATION OF 4.9968 g OF OLD SYDNEY COLLIERIES AT 150°C
7.0 g of KOH was used as "water gas absorbent".

Time (h)	$t^{0.60}$	P_t *(mm)*
0.00	0.00	763.5
0.166	0.34	745.5
0.333	0.52	734.0
0.500	0.66	723.3
0.666	0.78	714.1
0.833	0.90	705.3
1.00	1.00	698.3
1.25	1.14	686.3
1.50	1.28	674.7
1.75	1.40	663.4
2.00	1.52	652.2
2.50	1.73	629.9
2.75	1.84	619.3
3.00	1.93	608.1
3.75	2.21	577.0
4.25	2.38	556.5
4.75	2.55	536.2
5.25	2.70	516.0
5.75	2.86	496.0
6.25	3.00	476.7
6.75	3.15	457.5
7.25	3.28	439.2
7.75	3.42	421.2
8.25	3.55	405.0
8.75	3.68	389.4

TABLE 2

WESTERN DOMINION KLIMAX LIGNITE

Symbol	*Temp. (°C)*	*Wt. of coal*	B_s *(graph)*	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	K_s $(h^{-1}) \times 10^4$
◬	115	4.9991	734	0.5331	6.3	2.10
⊙	120	3.9940	750.8	0.5400	10.0	4.57
◬	125	4.9950	700	0.4956	9.8	4.40
⊙	130	3.9939	762	0.5336	11.7	5.90
◬	135	4.9992	720	0.4973	10.6	5.00
⊙	140	4.9978	672	0.4590	19.0	13.4

TABLE 3

S. J. DOUCETTE

Symbol	*Temp.* (°C)	*Wt. of coal*	B_x (*graph*)	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	K_s (h^{-1}) × 10^4
⊙	120	4.9968	760	0.5514	5.9	1.89
△	125	4.9991	754	0.5339	5.4	1.60
⊙	130	4.9970	764	0.5348	8.7	3.59
△	135	4.9995	760	0.5249	11.3	5.70
⊙	140	4.9977	772.6	0.5276	13.3	7.35
△	145	4.9996	770	0.5191	16.0	10.0
⊙	150	4.9973	816	0.5501	25.4	21.7

TABLE 4

OLD SYDNEY COLLIERIES

Symbol	*Temp.* (°C)	*Wt. of coal*	B_x (*graph*)	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	K_s (h^{-1}) × 10^4
△	125	4.9960	774	0.5621	5.9	1.9
⊙	130	4.9978	798	0.5646	7.7	2.9
△	135	4.9962	776	0.5360	7.8	3.0
⊙	140	4.9969	798	0.5509	10.7	5.1
△	145	4.9951	788	0.5313	11.4	5.7
⊙	150	4.9968	826	0.5569	15.8	9.9
△	155	4.9941	820	0.5399	17.2	11.0
⊙	160	4.9966	826	0.5448	20.6	15.0

TABLE 5

CARDIFF SMOKELESS LUMP

Symbol	*Temp.* (°C)	*Wt. of coal*	B_x (*graph*)	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	K_s (h^{-1}) × 10^4
△	125	4.9940	766	0.5424	2.0	3.2
⊙	130	4.9948	782	0.5534	3.3	7.3
△	135	4.9914	785	0.5422	3.9	9.6
⊙	140	4.9914	797	0.5503	5.0	14.0
△	145	4.9967	766	0.5164	5.8	19.0
⊙	150	4.9966	824	0.5555	8.2	32.9
△	155	4.9962	770	0.5070	8.0	32.0
⊙	160	4.9976	834	0.5493	11.5	88.0

TABLE 6

RED DEER VALLEY

Symbol	*Temp.* (°C)	*Wt. of coal*	B_w (*graph*)	*Wt. of* O_2	$K_s^{0.50} \times 10^3$	$K_s\ (h^{-1}) \times 10^4$
⊙	110	4.9934	752	0.5609	5.8	1.8
⊙	115	4.9950	752	0.5538	6.9	2.5
⊙	120	4.9920	754	0.5481	8.1	3.2
⊙	125	4.9926	758	0.5441	9.4	4.2
⊙	130	4.9896	757	0.5366	10.0	4.9
⊙	135	4.9896	755	0.5286	14.4	8.4

TABLE 7

CAIRNESS SEAM COAL

Symbol	*Temp.* (°C)	*Wt. of coal*	B_w (*graph*)	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	$K_s\ (h^{-1}) \times 10^4$
⊙	150	4.9970	774	0.5229	3.0	6.1
⊙	160	4.9978	790	0.5213	4.2	11.0
⊙	170	4.9975	806	0.5197	6.5	22.0

TABLE 8

SHAUGNESSY

Symbol	*Temp.* (°C)	*Wt. of coal*	B_w (*graph*)	*Wt. of* O_2	$K_s^{0.60} \times 10^3$	$K_s\ (h^{-1}) \times 10^4$
⊙	120	4.9934	752	0.5466	5.6	1.7
⊙	125	4.9950	752	0.5397	6.7	2.4
⊙	130	4.9920	754	0.5346	7.9	3.1
⊙	135	4.9896	757	0.5300	9.2	4.0
⊙	140	4.9896	757	0.5237	10.2	4.7
⊙	145	4.9896	755	0.5160	14.1	8.1

Expressing eqn (1) on a unit basis with respect to the weight of coal and pressure of oxygen, it becomes:

$$\frac{-1}{W}\cdot\frac{\mathrm{d}P_i}{\mathrm{d}t}=\frac{K_s''\left[\frac{P_i}{W}\cdot\frac{B_1}{B_w}+B_1-\frac{B_1}{W}\right]}{\left[\frac{B_w-P_i}{B_w W}\right]^{0.50}} \tag{2}$$

where: B_1 = effective initial pressure for 1 g, and is equal to P_0+b_w/W.

Thus P_i for 1 g, $B_1 - \frac{B_1}{W}\cdot\frac{P_i}{W}(B_1/B_\infty)$ for any P_i.

From eqn (2):

$$\frac{-\mathrm{d}P_i}{\mathrm{d}t} = \frac{K_s''\cdot\left[P_i\frac{B_1}{B_\infty} + B_1 W - B_1\right]\cdot(B_\infty W)^{0.50}}{(B_\infty - P_i)^{0.50}} \tag{3}$$

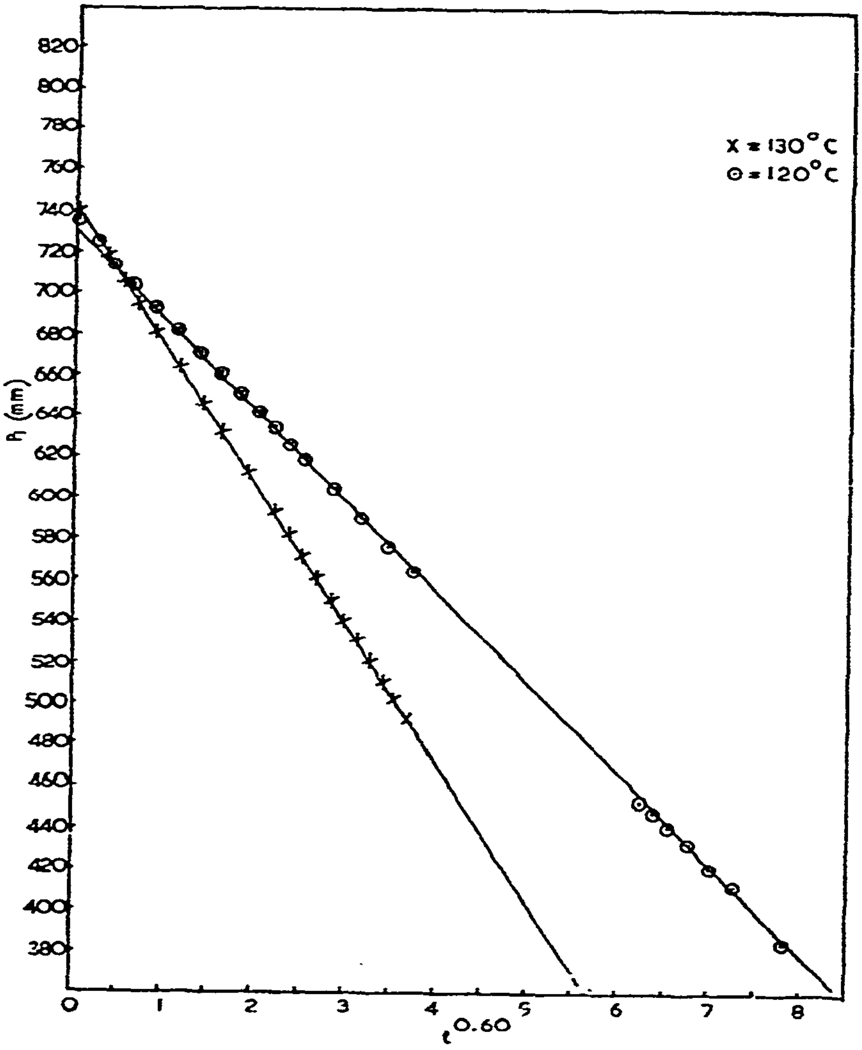

Fig. 3. P_i vs. $t^{0.60}$ Western Dominion Klimax Lignite.

On integration, re-arrangement, expansion of the resulting logarithmic term and subtracting,

$$2\left(\frac{B_x-P_i}{B_x W}\right)^{0.50}\text{, yields}$$

$$\frac{2}{3}\left(\frac{B_x-P_i}{B_x W}\right)^{3/2}\left[1+0.60\left(\frac{B_x-P_i}{B_x W}\right)+0.43\left(\frac{B_x-P_i}{B_x W}\right)^{2}+\right]=K_s\frac{B_1}{B_x}t+C \qquad (4)$$

as a first approximation.

It has been shown that the constant of integration, C, is zero or negligibly small[3].

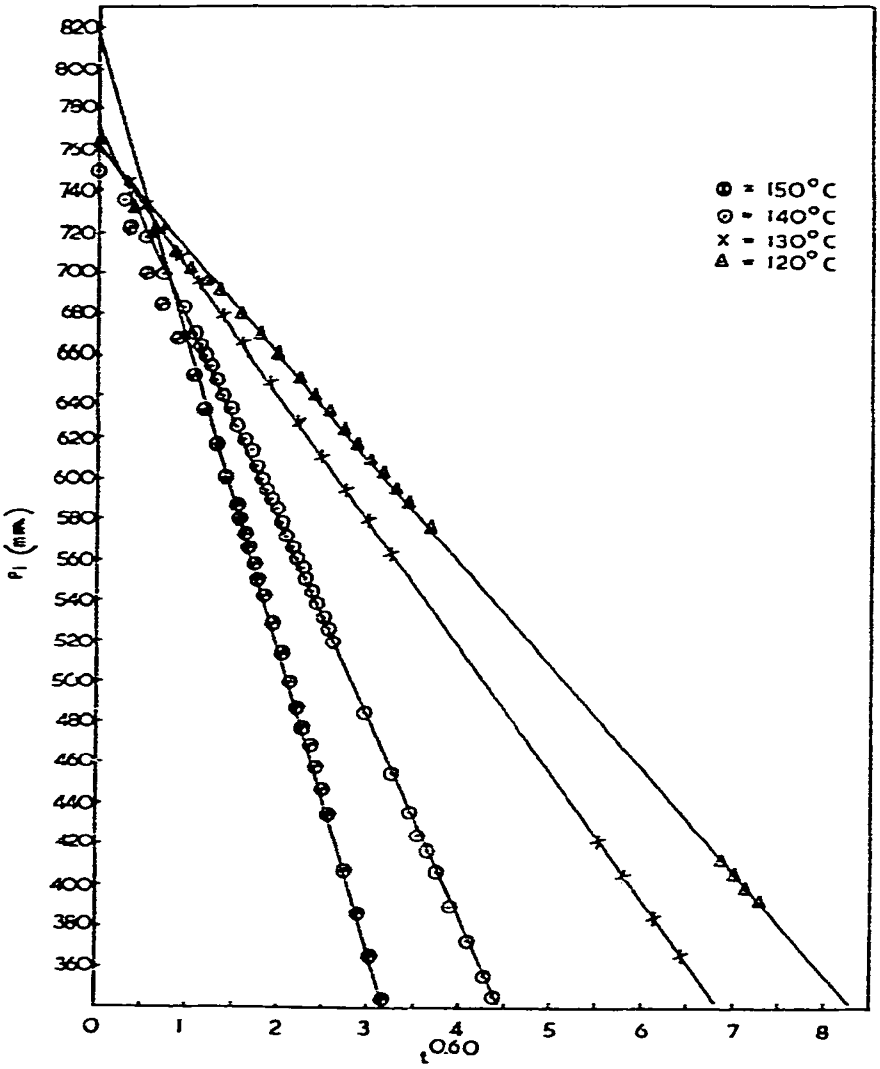

Fig. 4. P_i vs. $t^{0.60}$ S. J. Doucette.

Consequently, a relationship is readily obtained for pressures P_{i1} and P_{i2} at times t_1 and t_2.

It was also found that the logarithmic term was convergent, and therefore eqn (4) reduces to:

$$\left[\frac{B_w - P_i}{B_w}\right]^{1.67} \simeq K_s' t$$

$$\therefore \quad \frac{B_w - P_i}{B_w} = [K_s' t]^{0.60}$$

$$\therefore \quad P_i = [K_s' t]^{0.60} B_w + B_w$$

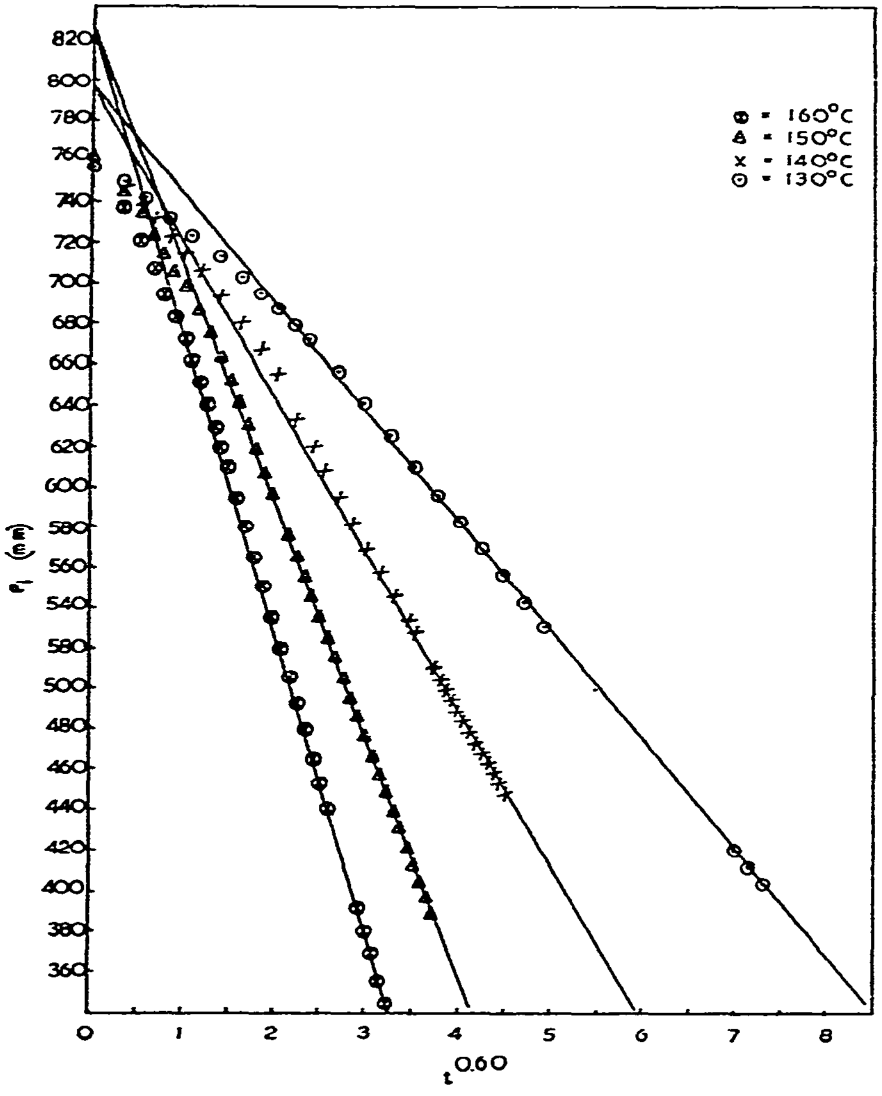

Fig. 5. P_i vs. $t^{0.60}$ Old Sydney Collieries.

or $$P_i = B_\infty[K_s]^{0.60}\cdot t^{0.60} + B_\infty \tag{5}$$

A plot of P_i vs. $t^{0.60}$ yields a straight line with a slope of

$$B_\infty(K_s^n)^{0.60}$$

and intercept on the P_i axis $= B_\infty$ at zero time.

Let M_0 and W_0 be the initial weights of oxygen and coal, respectively. Then from the relationship[1]

$$\left[\frac{B(1)-P_i(1)}{B_1}\right] = \frac{M_0}{W_0}\left[\frac{B_\infty - P_i}{B_\infty}\right] \tag{6}$$

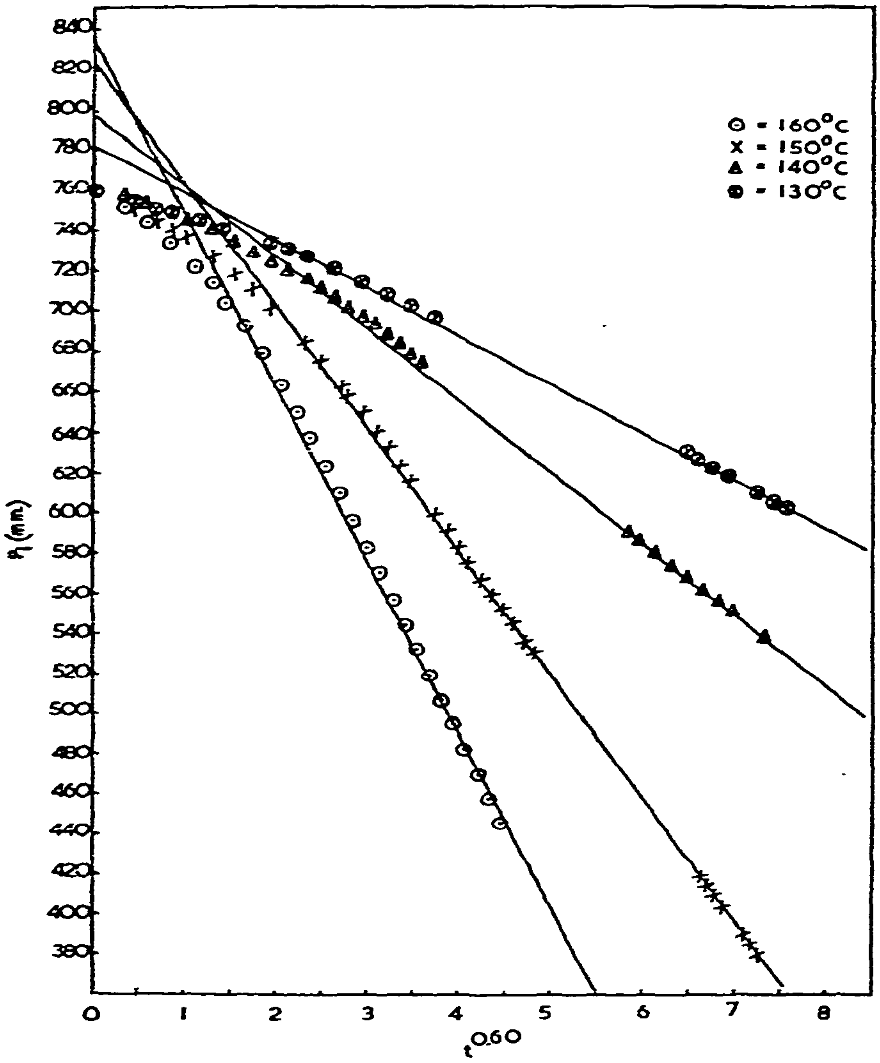

Fig. 6. P_i vs. $t^{0.60}$ Cardiff Smokeless Lump.

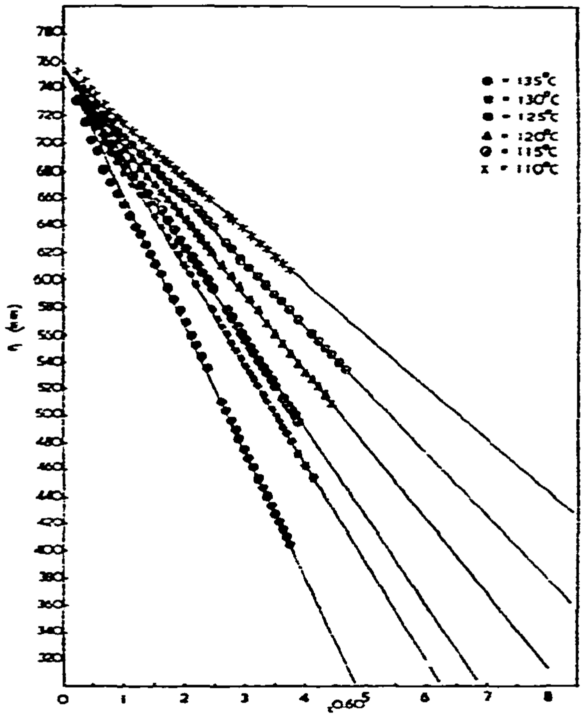

Fig. 7. P_i vs. $t^{0.60}$ Red Deer Valley.

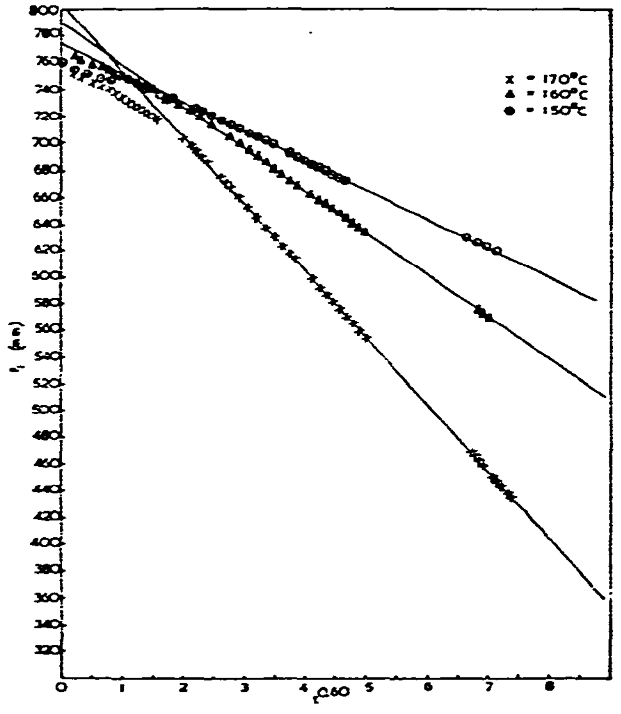

Fig. 8. P_i vs. $t^{0.60}$ Cairness Seam.

it can be shown that $$K_s = \left[\frac{\text{slope}}{B_\infty}\cdot\frac{M_0}{W_0}\right]^{1.67} \tag{7}$$

The specific reaction rate constants were found from eqn (5). These values which are shown in Tables 2–8 were calculated from eqn (7). The slopes were obtained from Figs. 3–10.

A typical calculation to demonstrate this method is given for 'Old Sydney Collieries' at 150°C. The data are shown in Table 1 and represented in Fig. 5.

$$\text{Slope} = \frac{708-600}{1.92-1.00} = 117.4\ \text{mm h}^{-0.60}$$

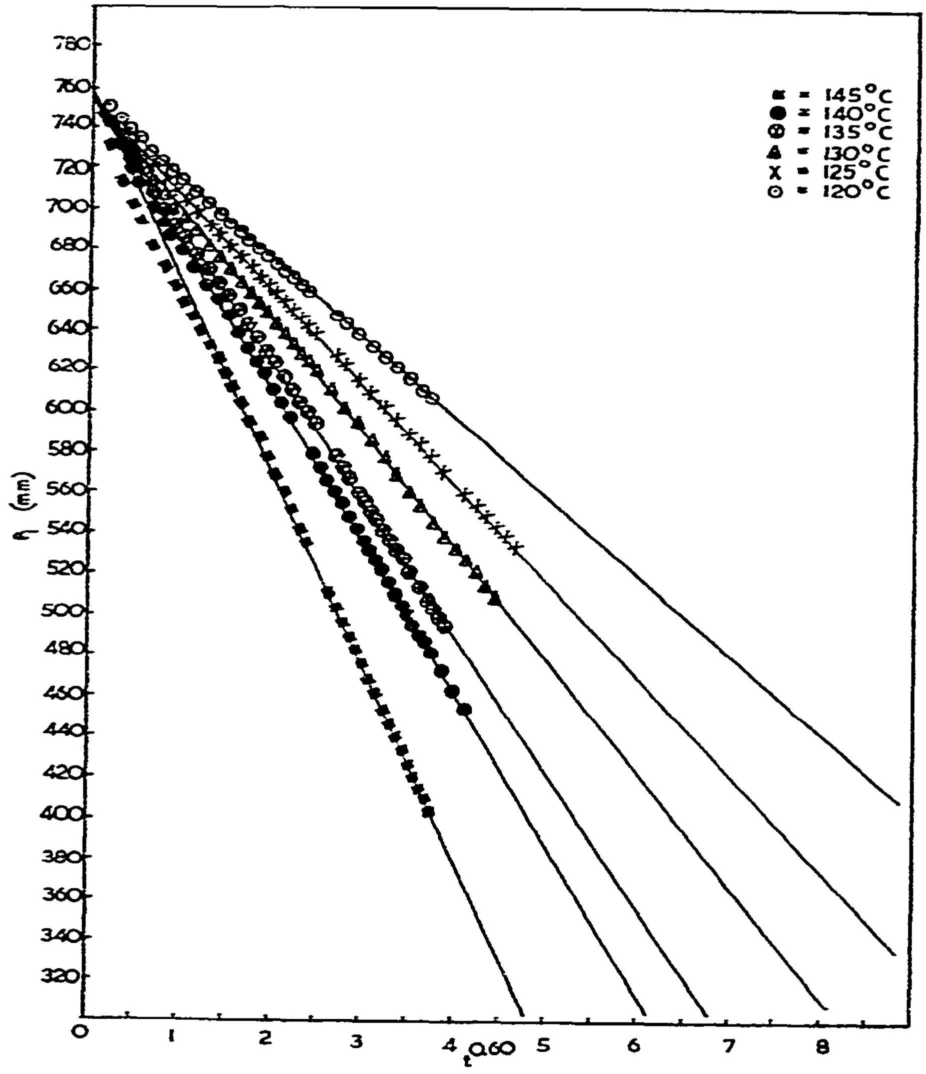

Fig. 9. P_t vs. $t^{0.60}$ Shaughnessy Coal.

$$B_\infty = 826 \text{ mm}$$

$$PV = \frac{W}{M} RT = \frac{M_0}{M} RT \qquad \therefore \quad M_0 = \frac{PVM}{RT}$$

$$= \frac{826}{760} \cdot \frac{556 \times 32}{82.1 \times 423} = 0.5569 \text{ g}$$

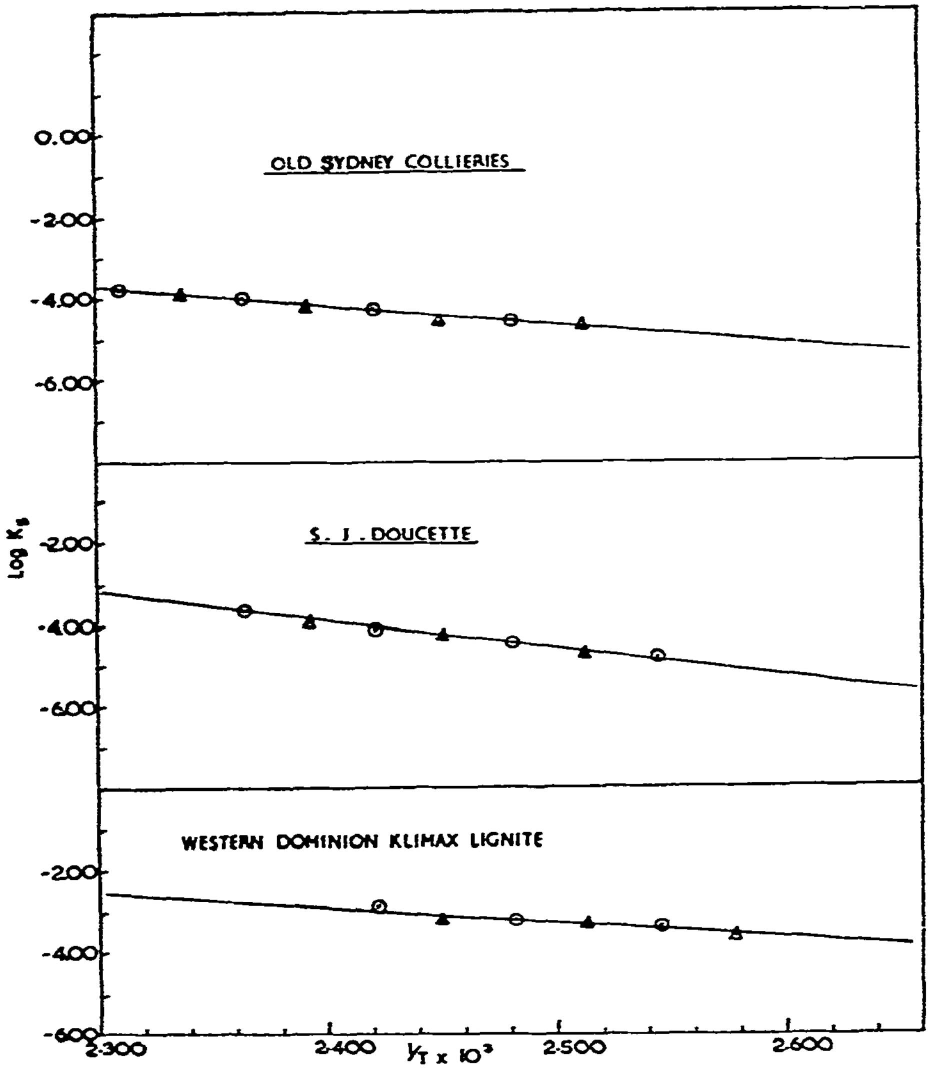

Fig. 10. Log K vs. $1/T \times 10^3$ for: Old Sydney Collieries (top); S. J. Doucette (middle); and W. D. K. Lignite (bottom).

The original weight of coal, $W_0 = 4.9968$ g

$$\therefore \quad K_s^{0.60} = \frac{\text{slope}}{B_x} \cdot \frac{M_0}{W_0}$$

$$= \frac{117.4 \times 0.5569}{826 \times 4.9968} = 1.58 \times 10^{-2}\ \text{h}^{-0.60}$$

$$\therefore \quad K_s = [1.58 \times 10^{-2}]^{1.67} = 9.85 \times 10^{-4}\ \text{h}^{-1}$$

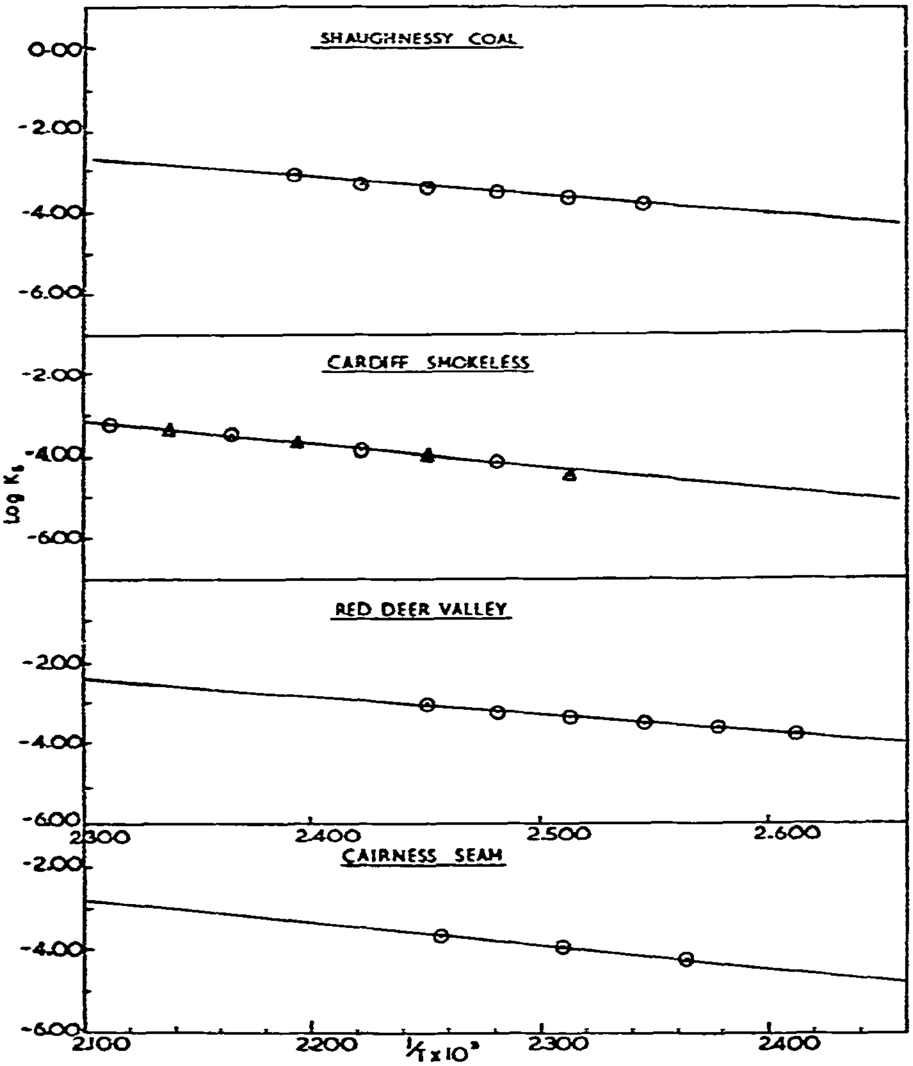

Fig. 11. Log K vs. $1/T \times 10^3$ for: Shaughnessy (top); Cardiff Smokeless; Red Deer Valley; and Cairness Seam (bottom).

Results

The energy of activation, ΔE, was obtained from the plot of the specific reaction rate constant, K_s, against $1/T$, and applying the usual equation, i.e. $\Delta E = -2.303 R$ slope. The results are shown in Figs. 10 and 11 and in Table 9.

TABLE 9

ΔE (kJ mol^{-1}) OBTAINED BY JONES[2] AND THE AUTHOR USING THE K_s VALUES OF BOTH WORKERS

The graphs from which the latter were calculated are shown in Figs. 10 and 11. The Arrhenius equation was used.

Type of coal	*Jones'*	*Author's (and Jones')*
Western Dominion Klimax Lignite	73.64	74.68
S. J. Doucette	129.6	130.2
Old Sydney Collieries	76.57	78.53
Cardiff Smokeless Lump	100.6	102.5
Red Deer Valley		82.05
Cairness Seam		103.4
Shaughnessy Coal		85.10

Discussion

Table 9 shows the energy of activation values obtained for the analyses of four coals by Jones[2], and seven by the author, four of which were those done by the previously mentioned worker using the same apparatus and general procedures. We both used the kinetic equation developed by Piercy et al.[1] to interpret and calculate our results.

A comparison of these results indicates a consistency. They are of similar magnitude, and compare well with those of other workers[1,4] and within the reliable allowable limits given by Mayers[5] for the oxidation of varying ranks of coal.

The average K_s values were found to be of quite similar magnitude as those of Piercy et al.[1] and Jones[2]. Similar agreement was found for B_∞ values obtained from the graphs.

It is therefore concluded that these results are reproducible, and that the kinetic equation as published in ref. 1 is valid for use in such oxidation reactions. This equation was applied successfully to varying ranks of coals, and the only factor which tends to shed some doubt on its applicability is encountered in the B_∞ values (see Figs. 4 and 6) for Cardiff Smokeless and Cairness Seam coals, respectively.

In all other examples the initial rate of sorption of oxygen is rapid, and the initial pressure of oxygen, P_0, could not be accurately determined. In the two cases mentioned, the initial sorption was relatively slow. The question arises whether B_∞ holds for these or whether P_0 is more suitable. It is the author's opinion that, although the original sorption is apparently small, a significant amount of oxygen was sorbed. Furthermore, since in the case of Cardiff Smokeless Lump two workers at different times and working at different temperatures obtained B_x values which were quite similar, and which when used in further calculations resulted in comparatively close K_s and ΔE values, it is suggested that this method is satisfactorily applicable here.

It appears that the process is a pure chemical sorption of oxygen. If the process were diffusion-controlled, the energy requirement would certainly have led to a smaller energy of activation.

CONCLUSION

The results obtained from this study are extensive enough to establish the validity of the original equation published in ref. 1.

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