Comments to the preceding letter by Alderibigbe and Szekely

I have gone over the communication on "The Temperature Dependence of the Rate Constants $K_1$, $K_2$, and $K_3$ in the Langmuir-Hinshelwood Rate Relation for Carbon-Carbon Dioxide Reaction." The gasification rate must always be equal to $j_0\theta$. The thing which, of course, determines the gasification rate at a particular temperature is $\theta$. The lower $\theta$, the lower the gasification rate.

The gasification rate will only be equal to (or approach closely) $i\psi(1-\theta)P_{CO}$, when $j_0\theta > j_0p_{CO}$ or $j_0 > j_0p_{CO}$. This is, in fact, true if $p_{CO}$ is small enough. But if $p_{CO}$ is to be small at temperatures where gasification is proceeding at a significant rate, $p_{CO}$ also needs to be small. In this case the gasification rate can be given by either

$$\text{Rate} = i\psi(1-\theta)P_{CO} = j_0\theta$$

and since $\theta$ is small

$$\text{Rate} = i\theta p_{CO} = j_0\theta.$$ 

In fact, we have shown in the Biederman et al. paper in Carbon 14, 311 (1976) that the equation, $\text{Rate} = i\theta p_{CO}$, is operative at low $p_{CO}$ and, hence, low $p_{CO}$ pressures. The equation, $\text{Rate} = j_0\theta$, must also be operative.

Therefore, I do not agree that when the forward step

$$\text{C}_1 + \text{CO}_2 \rightarrow \text{CO} + \text{C}(O)$$

is slow compared to $\text{C}(O) \rightarrow \text{CO}$ the over-all gasification rate is necessarily given by

$$(i) i = j_0 p_{CO}$$

that is, your eqn (8). As just discussed, it depends upon the relative rates of

$$j_0 p_{CO}$$

and

$$j_0 \theta.$$ 

In fact, this is what the conventional Langmuir-Hinshelwood rate expression for the C-CO$_2$ reaction is saying. Therefore, the fact that $E_1 > E_2$ does not necessarily invalidate the conventional form of the Langmuir-Hinshelwood rate expression.

Another way to look at it is that $K_{P_{CO}}$ will be $< 1$ if the rate $=i\theta p_{CO}$. In this case, eqn (9) reverts back to the standard form of the Langmuir-Hinshelwood equation.

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P. L. Walker, Jr.

Reply of the authors to the comments by P. L. Walker, Jr.

The preceding letter has certainly been thought provoking. We fully agree that the gasification rate must equal $j_0\theta$. However, it is rather less obvious that the gasification rate can equal or approach

$$i(1-\theta)P_{CO}, \text{i.e. eqn (8)}$$

in our paper only when

$$j_0\theta > j_0p_{CO} \text{ or } j_0 > j_0p_{CO}.$$ 

This is an important point, because it is crucial to the rest of the argument put forward in your letter. Let us consider the above contention in detail:

$$j_0 > j_0p_{CO} \text{ or } \frac{1}{P_{CO}} > \frac{i}{j_0 p_{CO}} = \frac{i}{j_0 p_{CO}} \frac{P_{CO}}{P_{CO}}$$

(1)

Upon examining Fig. 1 in the Strange and Walker article, it is seen that a linear relationship is being obtained between the gasification rate and the partial pressure of CO$_2$ (for fixed $CO/CO_2$ ratio) for the conditions given in Table 1. If we now proceed to substituting numerical values into eqn (2), e.g. using the entry corresponding to

$$T = 952^\circ C, P_{CO}/P_{CO_2} = 0.0975, P_{CO_2} = 80 \text{ Torr}$$

we find that under these conditions the quantities

$$\frac{i}{j_0 p_{CO}}$$

or

$$\frac{1}{P_{CO}} > \frac{i}{j_0 p_{CO}} \frac{P_{CO}}{P_{CO}}$$

(2)