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Comments to the preceding letter by Alderibigbe and Szekely

I have gone over the 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 $j_3\theta$. The thing which, of course, determines the gasification rate at a particular temperature is θ. The lower θ, the lower the gasification rate.

The gasification rate will only be equal to (or approach closely) $i_1(1-\theta)P_{CO_2}$ when $j_3\theta \gg j_1\theta p_{CO}$ or $j_3 \gg j_1 P_{CO}$. 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_2} also needs to be small. In this case the gasification rate can be given by either

$$\text{Rate} = i_1(1-\theta)P_{CO_2} = j_3\theta$$

and since θ is small

$$\text{Rate} = i_1 p_{CO_2} = j_3\theta.$$

In fact, we have shown in the Biederman *et al.* paper in Carbon **14**, 351 (1976) that the equation, Rate $= i_1 p_{CO_2}$, is operative at low p_{CO_2} and, hence, low p_{CO} pressures. The equation, Rate $= j_3\theta$, *must* also be operative.

Therefore, I do not agree that when the forward step

$$C_f + CO_2 \xrightarrow[i_1]{} CO + C(O)$$

is slow compared to

$$C(O) \longrightarrow CO$$

the over-all gasification rate is necessarily given by

$$(i_1)(C_f)(p_{CO_2})$$

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

$$j_1\theta p_{CO}$$

and

$$j_3\theta.$$

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 is $>E_3$ does not necessarily invalidate the conventional form of the Langmuir–Hinshelwood rate expression.

Another way to look at it is that $K_2 p_{CO}$ will be $\ll 1$ if the rate $= i_1 p_{CO_2}$. In this case, eqn (9) reverts back to the standard form of the Langmuir–Hinshelwood equation.

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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 $j_3\theta$. However, it is rather less obvious that the gasification rate can equal or approach

$i_1(1-\theta)P_{CO_2}$ i.e. eqn (8) in our paper only when

$j_3\theta \gg j_1\theta P_{CO}$ or $j_3 \gg j_1 P_{CO}$.

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:

$$j_3 \gg j_1 P_{CO} \tag{1}$$

dividing both sides by $j_3 P_{CO_2}$ we have

$$\frac{1}{P_{CO_2}} \gg \frac{j_1}{j_3}\frac{P_{CO}}{P_{CO_2}}$$

or

$$\frac{1}{P_{CO_2}} \gg k_2 \frac{P_{CO}}{P_{CO_2}}. \tag{2}$$

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 ratios) 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

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

we find that under these conditions the quantities

$$\frac{1}{P_{CO_2}} \text{ and } K_2\frac{P_{CO}}{P_{CO_2}}$$