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Comments to the preceding letter by Alderibige and Szekeley

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 $j_3 \gg j_1P_{CO}$. 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

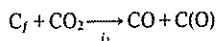
$$\text{Rate} = i_1(1-\theta)P_{CO_2} = j_3\theta$$

and since θ is small

$$\text{Rate} = i_1P_{CO_2} = j_3\theta.$$

In fact, we have shown in the Biederman *et al.* paper in *Carbon* 14, 351 (1976) that the equation, $\text{Rate} = i_1P_{CO_2}$, is operative at low P_{CO_2} and, hence, low P_{CO} pressures. The equation, $\text{Rate} = j_3\theta$, must also be operative.

Therefore, I do not agree that when the forward step



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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 $j_3 \gg j_1P_{CO}$.

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:

$$j_3 \gg j_1P_{CO} \quad (1)$$

dividing both sides by $j_3P_{CO_2}$, we have

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

is slow compared to



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

$$j_3\theta P_{CO}$$

and

$$j_3\theta.$$

In fact, this is what the conventional Langmuir-Hinshelwood rate expression for the C-CO₂ 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_2P_{CO} will be $\ll 1$ if the rate $= i_1P_{CO_2}$. In this case, eqn (9) reverts back to the standard form of the Langmuir-Hinshelwood equation.

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or

$$\frac{1}{P_{CO_2}} \gg k_2 \frac{P_{CO}}{P_{CO_2}} \quad (2)$$

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 CO₂ (for fixed CO/CO₂ 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

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

we find that under these conditions the quantities

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