APPENDIX II

Consider the following very simple surface reaction in which two diatomic molecules adsorb and then interact to form products. One molecule, A₂, adsorbs molecularly while the other, B₂, adsorbs dissocia-tively. The sequence is as follows:

$$A_2 + Ru \not RuA_2$$

 $B_2 + 2Ru \not 2RuB$
 $uA_2 + RuB → Products$

Using the Langmuir surface equilibrium approach gives the following expressions for the fractional coverages of the intermediates

R

$$[RuA_{2}] = K_{A}[A_{2}][Ru]$$

$$[RuB] = (K_{B}[B_{2}])^{1/2}[Ru]$$

$$[Ru] = 1/\{1 + K_{A}[A_{2}] + (K_{B}[B_{2}])^{1/2}$$

The last step is the rate limiting step so that the rate may be expressed as follows:

Using the above expressions for the intermediates leads to the following rate expression?

Rate =
$$\frac{kK_{A}(K_{B}[B_{2}])^{1/2}[A_{2}]}{\{1 + K_{A}[A_{2}] + (K_{B}[B_{2}])\}^{2}}$$

Note that the maximum order of the diatomic that dissociated is ± 0.5 . This is a general result and will be the same as long as the product contains only one atom of B. This is the case in the formation of $CH_{\frac{1}{2}}$ from CO. Several times throughout this thesis reference was made to the fact that this reaction follows Langmuir-Hinshelwood kinetics. This means that the rate limiting step of the mechanism involves the interaction of two adsorbed intermediates. Both reactants are competing for the same surface sites. Rideal-Eley kinetics result from a sequence in which the rate limiting step involves the interaction of an adsorbed intermediate with a gas phase molecule.