8. MADIX, R. J., AND BOUDART, M., *J. Catalysis* 7, 240 (1967).
9. ALLEN, F. G., *J. Phys. Chem. Solids.* 8, 119 (1959).
10. EISINGER, J., AND LAW, J. T., *J. Chem. Phys.* 30, 410 (1959).
11. SCHLIER, R. E., AND FARNSWORTH, H. E., *J. Chem. Phys.* 30, 917.

E. J. NOWAK
J. M. DECKERS
M. BOUDART*

Princeton University
Princeton, New Jersey†

Received February 29, 1968; revised April 10, 1968

* To whom correspondence should be addressed; present address: Department of Chemical Engineering, Stanford University, Stanford, California 94305.

† This work was supported by the National Science Foundation.

Statistics of Site Trapping in Adsorption of Triatomic Molecules

It is known that random adsorption of diatomic molecules on adjacent pairs of surface sites will, if the adlayer is immobile, lead to the trapping of a fraction of the surface as single sites not available for adsorption. Roberts (*1*) has estimated this fraction as 8% for both square and close-packed arrangements of surface lattice sites. The analogous result for triatomics does not seem to be available, but is of interest in the interpretation of the low coverages reached (*2, 3, 4*) in the adsorption of CO_2 on metal films. In some cases it is found that less than 50% of the surface sites can be filled, even though the differential heat of adsorption may be quite large at the highest coverages reached (*3*). Since it is possible to achieve complete coverages of O_2 or CO on similar surfaces (*5*) it seems unlikely that steric effects due to the size of the molecule are important. A possible explanation of the low CO_2 coverages would be site trapping due to formation of an immobile adsorbed layer.

We report here the results of a computer investigation of the trapping of vacant sites by immobile adsorption of triatomics on square and close-packed plane lattices. A triatomic molecule might occupy three adjacent sites in either a linear or triangular configuration. We have investigated layers of each configuration alone, and also randomly mixed layers having equal probabilities for the two configurations.

The procedure used was to set up in computer storage a two-dimensional array of storage locations, one for each surface site, and to record in the appropriate location the state of each site. Storage for the close-packed lattice was organized according to the strategy of Dean (*6*). Initially all sites were recorded as vacant. Random numbers were then generated to select a surface site. If this site was found to be already filled, the trial was rejected. If it was vacant, further random numbers were generated to select the configuration, for a mixed layer, and one of the possible orientations on the surface. The two neighboring sites defined by the configuration and orientation thus selected were examined for occupation. If both were vacant, the trial was successful, and all three sites were recorded as filled; otherwise the trial was rejected. This procedure was repeated until a large number of trials led to no further filling. All the sites were then investigated systematically for all possible orientations, and any triple vacancies consistent with the chosen configuration were filled. The final coverage so obtained was taken as that which would have been reached in an infinite number of strictly random trials. Provided at least 90% of the

final coverage was achieved in the random process, this procedure appeared to be satisfactory in that a more extended random phase did not significantly alter the results. In all cases toroidal boundary conditions were assumed.

The results of the calculations are shown in Table 1, which gives the average fractional coverage reached for each combination of configuration and lattice, together with its standard deviation. These are averages of ten computer runs on a 50×50 lattice in each case. A few runs on smaller lattices gave similar results with larger standard deviations.

TABLE 1
RESULTS OF CALCULATIONS

Lattice	Configuration	Coverage	Std. deviation
Square	Linear	0.877	0.006
Square	Triangular	0.836	0.006
Square	Mixed	0.864	0.005
Close-packed	Linear	0.834	0.006
Close-packed	Triangular	0.797	0.005
Close-packed	Mixed	0.861	0.004

As can be seen from the table, coverages of 80–90% are reached, with small differences depending on the configuration and lattice geometry assumed. In no case is more than 20% of the surface trapped as bare sites. Site trapping might therefore be an explanation of the finding of Collins and Trapnell (*2*) that CO_2 appears to occupy four sites on W, Mo, and Fe, but cannot explain the lower coverages found in other systems (*3*, *4*).

REFERENCES

1. ROBERTS, J. K., *Proc. Roy. Soc.* (*London*) **A152**, 472 (1935).
2. COLLINS, A. C., AND TRAPNELL, B. M. W., *Trans. Faraday Soc.* **53**, 1476 (1957).
3. HAYWARD, D. O., AND TRAPNELL, B. M. W., "Chemisorption," p. 245. Butterworths, Washington, 1964.
4. QUINN, C. M., AND ROBERTS, M. W., *Trans. Faraday Soc.* **58**, 569 (1962).
5. LANYON, M. A. H., AND TRAPNELL B. M. W., *Proc. Roy. Soc.* (*London*) **A227**, 387 (1955).
6. DEAN, P., *Proc. Cambridge Phil. Soc.* **59**, 397 (1963).

IAN D. GAY

From the Department of Chemistry
Simon Fraser University
Burnaby 2, B. C. Canada

Received April 2, 1968