

Thus if the location of the home of individual  $i$  is  $z_i$  and if the onset of the disease occurred at time  $t_i$ , then  $X_{ij}=1$  if  $|z_i-z_j|<\delta$  and  $|t_i-t_j|<\tau$ , and  $X_{ij}=0$  otherwise. (In practice Knox chose  $\delta=1$  kilometre and  $\tau=60$  days.) If the disease is not contagious, then one should not expect the events  $|z_i-z_j|<\delta$  and  $|t_i-t_j|<\tau$  to occur together except by pure chance. However, if the disease is contagious, then one would expect these pairs of events to be linked more frequently than would occur simply by chance, and if such a pair of events occurred together, one would be tempted to say that one individual, being in the right place at the right time, caught the disease from the other. A large value of  $X$  then, is evidence of clustering. To find out what is a large value of  $X$ , one evaluates the distribution  $X$  when the times ( $t_1, t_2, \dots, t_n$ ) are paired off at random with the locations ( $z_1, z_2, \dots, z_n$ )—thus eliminating space-time interactions.

Pike and Smith propose that each case has a period of susceptibility during which the onset of the disease occurs, and a period of infectivity during which he may pass on the disease to another individual. If  $T_j^s, T_j^i$  are the periods of susceptibility and infectivity respectively for the  $j$ th patient, and  $A_j^s, A_j^i$  are the areas of the  $j$ th patient's effective movements during his susceptible and infective periods respectively, then their statistic is  $Y=\sum Y_{ij}$  where  $Y_{ij}=1$  if  $T_j^s$

overlaps  $T_j^i$  and  $A_j^i$  overlaps  $A_j^s$ , and  $Y_{ij}=0$  otherwise. Again a large value of  $Y$  is evidence for clustering, and to find out how large is "large", the distribution of  $Y$  must be worked out when the time-pairs ( $T_1^s, T_1^i; T_2^s, T_2^i; \dots; T_n^s, T_n^i$ ) are paired off at random with the area-pairs ( $A_1^s, A_1^i; A_2^s, A_2^i; \dots; A_n^s, A_n^i$ ).

Pike and Smith have worked out the expected value and variance of  $Y$ , and O. Abe (*Ann. Math. Stat.*, **40**, 1: 1969) has shown that, for large  $n$ ,  $Y$  is normally distributed. Pike and Smith moreover have promised to rework the London data using their new test. It will be interesting to see if it produces a stronger result than their original one.

#### GAS EQUILIBRIUM

### Ammonium Chloride Molecules

THE simple view that ammonium chloride is completely dissociated when it sublimates into the gas phase was first challenged two years ago, when E. Clementi carried out a theoretical calculation of the electronic structure of the intact molecule and its dissociation products,  $\text{NH}_3$  and  $\text{HCl}$ , and predicted a minimum in the potential surface some 80 kJ per mole below the energy of the two products (*J. Chem. Phys.*, **46**, 3851; 1967). On this basis, intact molecules should account for about 0.15 per cent of the vapour at 528° K. This prediction has now been elegantly confirmed by P. Goldfinger and G. Verhaegen at the Laboratoire de Chimie Physique Moléculaire at the Free University, Brussels (*J. Chem. Phys.*, **50**, 1467; 1969). Yet another assertion of the elementary textbooks will evidently have to be discarded.

Goldfinger and Verhaegen have used a mass spectrometer to demonstrate that intact molecules exist in the gas phase. In these circumstances, intact  $\text{NH}_4\text{Cl}$  molecules would be expected to show up as  $\text{NH}_4^+$  ions—other experiments have shown that the molecules break up in this way on electron impact. Because of

the possibility of the confusion of  $\text{NH}_4^+$  with  $\text{H}_2\text{O}^+$  and  $^{15}\text{NH}_3$ , the hunt for intact molecules of ammonium chloride was carried out with the fully deuterated material  $\text{ND}_4\text{Cl}$ . Fortunately it has been possible to demonstrate that the isotopic substitution has very little effect on the heat of sublimation into completely dissociated material—close on 180 kJ per mole.

Goldfinger and Verhaegen seem confident that they have accurately distinguished between  $\text{ND}_4^+$  ions and other possible sources of ionic species with  $m/e=22$ . One immediate outcome of their measurements, which extend over a substantial range of temperature, is an estimate of the dissociation energy of the gas phase molecules which agrees well with the predictions of Clementi. Goldfinger and Verhaegen rightly point out that one of the most striking features of this tale is the quite remarkable accuracy of the original calculation of the electronic energy of the dissociating system, one of the most complicated systems to have been dealt with from first principles. The explanation seems to be that there is no change in the number of electron pairs in the system on dissociation, whether the intact molecule is considered as a hydrogen bonded system or as an ion pair  $\text{NH}_4^+\text{Cl}^-$ , which in turn implies that there is no large amount of electron correlation energy to complicate the balance between the intact and dissociated forms of  $\text{NH}_4\text{Cl}$ .

#### SALINITY MEASUREMENT

### Conductivity Displaces Titration

SINCE the turn of the century, oceanographers have measured the salt in their samples of seawater by performing silver nitrate titrations and by using empirical equations to relate chloride to total salt. The technique is tedious and not particularly accurate: recently, conductivity methods have become more usual. In an effort to standardize salinity determinations based on conductivity, UNESCO and the National Institute of Oceanography published a new operational definition of salinity in 1966.

A. J. Hill, the Chairman of the Hydrographical Committee of the International Council for the Exploration of the Sea, now says that this new definition has not diffused as fully as it might through the ranks of oceanographers. The definition invokes a conductivity ratio  $R_{15}$ , itself defined as the ratio of the conductivity of the water sample to that of water having a salinity of exactly 35 parts per thousand at 15° C and one standard atmosphere pressure. The salinity ( $S$ ) in parts per thousand, is then defined by a polynomial:

$$S = -0.08996 + 28.29720R_{15} \pm 12.80832R_{15}^2 - 10.67869R_{15}^3 + 5.98624R_{15}^4 - 1.32311R_{15}^5$$

Salinity so defined can be measured to  $\pm 0.003$  parts per thousand: the accuracy is of course dependent to some extent on the precise salt composition and  $p\text{H}$  of the water. Apparently many research projects are under way which exploit salinity measurements at this level of accuracy.

#### CHEMICAL MECHANISMS

### One Mechanism for Two

MORE than thirty years ago, Ingold developed the mechanisms of substitution by a negatively charged