

DISCUSSION

(pps.109 -112)

E. Schmidt. In Braunschweig we have decided to carry out sound dispersion tests at high temperatures; extensive preparatory work and complicated theoretical study are involved, to make sure that the apparatus will work.

Fromherz. In difficult conditions Damköhler's work clearly presents the relationship between reaction velocities and sound dispersion curves and exposes the theoretical possibilities of their application. As far as I can see, the determinant equations show in particular that the same final result can be achieved with different reaction velocities, especially if the reactions are of a complicated nature and their effect is mutually compensated. Mathematically this means that the functional relations between sound dispersion curves, reaction types and velocities are not univocal. This will apply particularly to the complicated combustion reactions.

Damköhler. But just in simple cases, e.g. with carbon dioxide at high temperatures one dissociation reaction, namely that of O_2 , amounted to very little, the main proportion of the sound dispersion was produced by the CO_2 dissociation.

Fromherz. In order to afford any deduction on reaction velocities, owing to its exceptional functional dependence on the prevailing reaction velocities the sound dispersion curve should be very accurately plotted. If the limit of accuracy of dispersion measurement exceeds a perceptible but still very small amount, the margin of error in reaction velocity determination is exceedingly high with the result that the figures thus obtained become very unreliable. I can think of a similar case, namely the relation between optical dispersion curves and frequencies and amplitudes of natural vibrations.

Damköhler. I don't agree; the main thing is to get a general impression of the curve shape and to measure the whole dispersion curve; and a certain sound frequency range characterises a given chemical reaction velocity. Even if one or other of the reaction velocities, which do not affect considerably the shape of the dispersion curve, is wrong, still other reaction velocities could be more exactly determined. In practice this point should be more accurately checked. Moreover there are corrections owing to deviations from the perfect gas law and similar effects. If these are to be exactly considered, exceptionally involved expressions will result. The correction for differences from ideal gases has already been used in sound dispersion measurements. It should however be borne in mind that if we want to investigate the dissociation dispersion, this correction is insufficient in the form then used. This mainly because we can no longer apply the equilibria in partial pressures, but we must use the activities, introducing the activation coefficients. In sound dispersion tests this point has so far been wholly neglected, which presumably was in order as there could be no difference between the activation coefficient of an excited molecule and that of an unexcited molecule. If on the other hand it is a question of generating completely new products, this factor will certainly affect results. Something appears clearly from the formulae obtained, which presumably has so far been insufficiently stressed in sound dispersion tests. Fundamentally something on molecular reaction velocity can be learnt from sound dispersion measurements. We have seen the appearance of determinants with $n + 1$ rows, where n was the number of thermodynamically independent empirical reaction velocities. The interesting

point from the standpoint of reaction kinetics is not the overall reaction velocity but the elementary reaction velocity, which can be deduced from the former only with certain additional hypotheses, such as the principle of microscopic reversibility or the like. Opinions may vary on the applicability of this principle, but the elementary reaction velocity cannot be determined without these additional assumptions.

Busemann. - I do not see why the maximum sound velocity is arrived at with c_p/c_v values, in which the equilibrium adjustment is negligible. How were the c_p/c_v values determined?

Damköhler. The c_p/c_v assumed by us is previously calculated for the prevailing equilibrium. The values of the various components of the mixture were calculated by statistical spectroscopic methods for the required temperature.

E. Schmidt. The values we used for c_p and c_v apply to a given equilibrium composition and a given temperature. This however does not take into account the variation of the composition and consequent heat of reaction due to the temperature rise; i.e. it is assumed that only the temperature climbs, without affecting the equilibrium.

Zeiso. In the measurement of combustion temperatures, the cracking reactions must also be considered. The calculation is relatively simple as long as it can be assumed that the degree of cracking is small. If however it is not, at high temperatures the question of mutual influence must be considered; this question is quite difficult for a simple case, e.g. $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ and it is even more difficult with an engine gas. Moreover it is very difficult to say anything on the composition of the gas mixture in the state of dissociation at a given temperature and pressure. One is conditional on the other; and I wanted to ask whether it is automatically included in your statement or whether you want to extend those equations to cover this region.

Damköhler. At first we did not deal with engine combustion, but with rather circumstantial calculations we computed the gas composition of dissociating CO_2 gas at various temperatures and pressures and estimated the probable shape of sound dispersion curves. Here are the numerical values for that gas composition: at 2,600° K and 1 atm total pressure the CO_2 partial pressure is still 0.75, 0.16 for CO, 0.08 for O_2 and 0.007 atm for O-atoms. Certain assumptions based on specific cases have therefore been necessary. We have considered less the question of the engine exhaust gases than other questions; at first we calculated the integral isentrope when a combustion gas is expanded from 40 to 1 atm. These processes occur for instance in making detonation measurements in pipes; in front of the detonation head there are pressures of say 40 atm., then follows an isentropic rarefaction fan followed in turn by the detonation wave; thus an expansion is obtained down to perhaps one atm. We wanted to see which isentropic exponent m must be used in the calculation; from the beginning it was clear that it could not be c_p/c_v but that it must be $m < c_p/c_v$. The kinetics of this expansion has perhaps another interest. Let us consider reaction propulsion, i.e. a rocket with combustion chamber and jets; the thrust is ultimately obtained from the combustion energy. The question is now: which proportion of the combustion energy can be utilized as thrust. In this case it is decisive whether during the exhaust process, which lasts a comparatively short time - 10^{-3} to 10^{-4} sec., the dissociation reactions reverse or not; in the combustion chamber initially we have in any case a high temperature and thus dissociation. The latter implies that part of the heat, i.e. of the combustion energy, is used to split molecules. This does not concern the technician, who wants mere thrust. The question is now whether these dissociation reactions reverse again

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during the exhaust. If they do so rapidly, the thrust obtained is more than if they don't. We can conclude that the study of the kinetics of these high temperature reactions has also a certain practical importance.