

sapphire windows. It was connected to a pressure intensifier by stainless steel capillary tubing and could be used to 8000 atm with petroleum ether containing 10 % paraffin oil as pressure medium. The pressure in the optical cell was measured in terms of the primary pressure on the intensifier which was calibrated to 6000 atm with a Bourdon gauge. The temperature of the cell was measured with a mercury thermometer sitting in a 2 in. deep hole and was controlled manually to  $\pm 0.1^\circ\text{C}$ . The solutions were contained in a small stainless steel cell.<sup>16</sup> For some solutions fresh polythene O rings and a fresh polythene plug were used for each measurement in order to avoid contamination.

Blank corrections were determined at each wave length and at each pressure, and, to allow for possible irreproducibility in assembling the cell, all measurements were taken relative to some wavelength at which the CT complex does not absorb (usually 600  $m\mu$ , sometimes 750  $m\mu$ ). This procedure was facilitated by using as a reference an optical path of the same geometry as the high-pressure path but empty and fitted with an iris diaphragm. Corrections for the absorption by the acceptor, when this overlapped the CT band, were determined at each pressure in separate experiments.

Neither  $\text{CH}_2\text{Cl}_2$  nor MCH freeze under the conditions used but some of the solutions containing relatively high concentrations of the heavier hydrocarbon donors sometimes solidified at the highest pressure. With MCH solutions the solubility of the CT-complex was sometimes exceeded at the higher pressure and the coloured complex crystallized out.

#### EVALUATION OF DATA

A first approximation to the mole fraction equilibrium constant  ${}^xK$  and the absorption coefficient  $\epsilon$  of the complex was obtained by the method of Benesi and Hildebrand.<sup>17</sup> A further approximation was found by using the exact equation,

$$\frac{x_a^0 x_d^0}{D} + \frac{DV}{\epsilon^2} = \frac{1}{{}^xK\epsilon} + \frac{1}{\epsilon}(x_a^0 + x_d^0), \quad (2)$$

in which  $x_a^0$  and  $x_d^0$  are the initial mole fraction of acceptor and donor respectively,  $D$  is the optical density at  $\nu_{\text{max}}$  corrected for the absorption by the pure components,  ${}^xK$  and  $\epsilon$  are the unknown mole fraction equilibrium constant and the absorption coefficient multiplied by the optical path length in cm. The molar volume  $V$  of the solution is assumed to be equal to that of the solvent. This equation was fitted to experimental data by a least-square method in which it is assumed that the second term on the left hand side is constant.<sup>18</sup> The difference between using this method and curve fitting the Benesi-Hildebrand equation was generally negligible.

The final adjustment of the constants was made by comparing calculated and observed values of the optical density directly<sup>10</sup> and minimizing  $\Sigma(D_{\text{calc.}} - D_{\text{obs.}})^2$  by a Simplex method.<sup>19</sup> This method was more reliable than the method of steepest descent which for these "noisy" data gave results which depended on the starting values of  ${}^xK$  and  $\epsilon$ .\*

Only 1 : 1 complexes are formed in our solutions according to published work.<sup>1</sup> CT-bands are characteristically broad and the  $\nu_{\text{max}}$  were estimated by taking the mean of the maxima of all the measurements on a particular system. The accuracy is usually greater at higher pressure due to the greater intensity of the bands. In systems involving CA, TNB, and PIC, the absorption by the acceptor overlaps the CT band and the optical density was corrected for this in order to find the  $\nu_{\text{max}}$  (see fig. 1).

The oscillator strength  $f$  of the CT-absorption could be evaluated directly, by graphical integration of the area under the absorption curve plotted on a wave number scale, only for a few systems (TCNE+NAP, CA+NAP, TCNE+BEN) because of the overlap of the absorption bands. In the other case,  $f$  was estimated from  $\epsilon_{\text{max}} \Delta\nu_{\frac{1}{2}}$ , where  $\Delta\nu_{\frac{1}{2}}$  is the band width at  $\epsilon = \frac{1}{2}\epsilon_{\text{max}}$ . If  $\Delta\nu_{\frac{1}{2}}$  could not be measured we used the empirical formula of

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Briegleb (ref. (1), p. 46) which takes account of the dissymmetry of the CT bands. The oscillator strength is then given by<sup>20</sup>

$$f = 4.319 \times 10^{-9} \int \epsilon dv = 10.36 \times 10^{-9} \epsilon_{\max}(v_{\max} - v_{\frac{1}{2}L}), \quad (3)$$

where  $v_{\frac{1}{2}L}$  is the half-height frequency at the red side of the maximum of the CT-band. Some values are shown as a function of pressure in fig. (4).

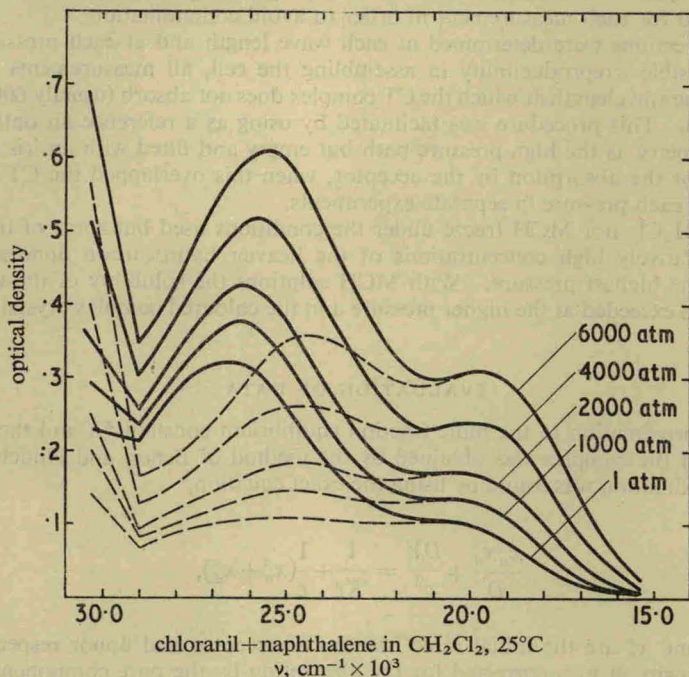


FIG. 1.—Absorption spectrum of CA+NAP complex in methylene chloride at various pressures. The dashed curves are corrected for CA absorption.

#### ERRORS IN $K$ AND $\epsilon$

The reliability of the best values of  $K$  and  $\epsilon$  can be calculated directly only if they are obtained by fitting a linear equation. Conrow *et al.*<sup>10</sup> devised one measure of the reliability of  $K$  derived from non-linear equation; instead, we calculated the standard deviation of the values obtained by fitting the Benesi-Hildebrand equation and these are given (expressed as %) in table 1. These deviations overestimate the uncertainty of the final values in the tables. A large uncertainty in  $^*K$  and  $\epsilon$  is, however, inherent in the method of finding both quantities simultaneously from optical density data. In many cases, limited solubility made it impossible to use the optimum experimental conditions<sup>10</sup> for the measurements.

The error in  $\epsilon$  directly enters into the estimate of the oscillator strength and adds to the uncertainty introduced by use of eqn. (3). For donors which form complexes with two CT-bands, the higher energy band is often completely hidden in the acceptor absorption and still further uncertainty is introduced, even into relative values of  $f$ , by possible changes in the relative intensities of the two bands.

The volume changes  $\Delta V$  associated with the formation of the CT complexes from their components can be calculated from the equilibrium constants by the equation

$$d \ln K/dP = -\Delta V/RT, \quad (4)$$

and are given by the slopes of curves such as shown in fig. 2. The uncertainty in  $\Delta V$  varies between  $\pm 0.5 \text{ cm}^3 \text{ mole}^{-1}$  to several  $\text{cm}^3 \text{ mole}^{-1}$  for the systems which gave less satisfactory  $K$  values.