With these expressions, the boundary layer equations can be integrated according to von Kármán to give approximate analytical solutions. The numerical coefficients are then obtained by comparison with the numerical solutions of the analogous heat transfer problems, corresponding to case I (3) and case II (4). The following results are obtained. They refer to cathodic deposition and anodic dissolution of metals. Details of the calculations will be published elsewhere.

Case I (limiting current density)

$$\begin{aligned} i_{\text{lim}} &= 0.499 \frac{zF}{1 \cdot t} D \Delta c \left( \frac{ga \Delta c}{D_{\text{T}} x} \right)^{1/4} \\ \delta_{d^{0.99}} &= 3.54 \left( \frac{Dvx}{ga \Delta c} \right)^{1/4} \\ \delta_{N} &= 0.57 \ \delta_{d^{0.99}}, \ \delta_{-} &= 0.55 \ \delta_{d^{0.99}} \\ u_{\text{max}} &= 1.0 \left( \frac{Dg \ a \Delta cx}{v} \right)^{\frac{1}{2}} \\ Nu_{x} &= 0.499 \ (ScGr_{x})^{1/4} \\ Nu_{\text{av}} &= \frac{4}{3} \ Nu_{h} = 0.665 \ (ScGr_{h})^{1/4} \end{aligned}$$

At the cathode  $c_e = 0$ , at the anode  $c_e = c_s$  under limiting current condition.  $i_{lim}$  is then the passivating c.d. at the anode.

Case II (normal electrolysis)

$$\begin{split} & \Delta c = 1.59 \ j \left( \frac{v \, x}{D^8 g \, a \, j} \right)^{1/5} \\ & \delta_{d \, 0 \cdot 99} = 3.09 \left( \frac{D^2 \, v \, x}{g \, a \, j} \right)^{1/5} \\ & \delta_N = 0.51 \ \delta_{d \, 0 \cdot 99} \\ & u_{\text{max}} = 1.1 \left( \frac{g \, a \, j}{v} \right)^{2/5} D^{1/5} \, x^{3/5} \\ & Nu_x = 0.558 \ (ScGr_x)^{1/4} \\ & Nu_{\text{av}} = \frac{6}{5} \ Nu_h = 0.670 \ (ScGr_h)^{1/4} \end{split}$$

In the presence of a conducting inert electrolyte, a correction term appears in a. The correction derived by Wilke and coworkers  $^2$  for case I is applicable also in case II.

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## Detection of Small Amounts of $\Delta^3$ -Carene in $\alpha$ -Pinene

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In connection with investigations on the sensitization of the skin to oil of turpentine  $^{1-3}$  it was necessary to detect small amounts of  $\Delta^3$ -carene in  $\alpha$ -pinene. Widmark  $^4$  has investigated the purity of various terpenes with the microsorption method according to Blohm  $^5$ . With this method he was able to show the index inhomogeneity of  $\alpha$ -pinene into which 0.2 % or more  $\Delta^3$ -carene had been added  $^6$ . When investigating the purity of various terpenes we have used the infrared spectrophotometry which has the advantage of being specific. As a criterion for purity we have used the spectra of the series of American Petroleum Institute Research Project 44\*.

In order to purify different terpenes, fractional distillation with Podbielniak-column and displacement chromatography were used. The latter method was more practicable giving equal or better results in shorter time. The displacement was performed on a macro scale by jointing together some columns with different diameters 7,8, in order to gain sharp fronts. The fractions were analyzed with infrared spectrophotometry 8,9. For detection of  $\Delta^3$ -carene in a-pinene the absorption peak of wave number 714 cm<sup>-1</sup> appeared to be most suitable and made it possible to show 0.39 %  $\Delta^3$ -carene (Fig. 1) with a liquid

<sup>\*</sup> Serial No. 566 for a-pinene, 567 for  $\beta$ -pinene, 1469 for  $\Delta^3$ -carene and 462 for d-limonene.

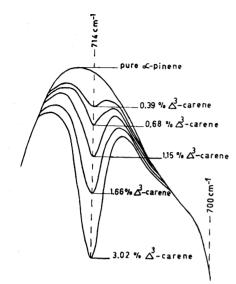


Fig. 1. A part of the infrared spectrum of  $\Delta^3$ -carene in  $\alpha$ -pinene with the peak at 714 cm<sup>-1</sup> (1.0 mm cell).

layer of 1.0 mm thickness. After enrichment by displacement chromatography 0.1 % of  $\varDelta^3$ -carene could be detected in some experiments. Silica gel and aluminium oxide were used as adsorbents. With both these adsorbents d-a-pinene and  $\varDelta^3$ -carene could be separated sharply from their mixtures. According to our observations, however, when using silica gel it must be taken into consideration, that the adsorbent, if too activated, tends to cause rearrangement of a-pinene.

Experimental part. Purification of a-pinene by chromatography.

20 ml of d-a-pinene (Variochem VVB Schimmel, Miltitz, Bz Leipzig,  $[a]_D + 38.42^\circ$ , distilled over sodium, infrared spectrophotometrically impure) was displaced by ethylalcohol with alumina (E. Merek, Darmstadt, standardised according to Brockmann) as adsorbent using a series of three columns (41  $300\pi + 11\ 000\pi + 4\ 500\pi\ mm^3$ ). Judging from the infrared spectra of the collected fractions, about 70 % of the input was free of impurities.

Purification of  $\Delta^3$ -carene by chromatography. The raw product of  $\Delta^3$ -carene (from EnsoGutzeit Oy, Finland) was rectified with Podbielniak-Skärblom-Linder-column <sup>10</sup> and a fraction, boiling range 170—171°C, was purified by displacement with ethyl alcohol using silica gel (Davison, 1 # Grade 922 Mesh Size T. 200, Davison Code No. 922—08-4X-1926) as adsorbent. Filters:  $2\ 200\pi + 1\ 000\pi$  mm³. The infrared spectra of the collected fractions showed that about 50 % of the input had at least 95% purity, comparing with the spectrum of  $\Delta^3$ -carene of the American Petroleum Institute.

Detection of small amounts of \( \Delta^3\)-carene in a-pinene. 20 ml of the mixture, which contained 0.1 %  $\Delta^3$ -carene in d-a-pinene was submitted to displacement using, as above, ethyl alcohol as the displacing agent and silica gel (Davison, 922-08-4X-1926) as the adsorbent.  $41\ 000\pi + 11\ 500\pi + 4\ 250\pi$  mm<sup>3</sup>. Filters: After 18.2 ml of the effluent had been collected, the next 0.4 ml (fraction 18.2-18.6 ml) gave the peak of △3-carene at 714 cm<sup>-1</sup> in the infrared spectrum. It could be calculated that about 18 % of the amount of 43-carene added to a-pinene was found in this fraction. Similar results were obtained using alumina as the adsorbent.

All infrared spectra were measured with a Perkin-Elmer Spectrometer Model 12-C equipped with a rock salt prism.

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