

The ratio of the concentrations of the gas and of the liquid in the mixture is

$$n(g)/n(l) = \eta_{rel} [M(l)/M(g)]^{1/2} i(g)/i(l),$$

where $i(g)/i(l)$ is the observed intensity ratio of the mass-spectral lines which characterise the gas and the liquid † respectively; η_{rel} is the relative sensitivity of the mass spectrometer towards the liquid and the gas; $[M(l)/M(g)]^{1/2}$ is a factor which accounts for the molecular flow regime in the capillary inlet system; $M(l)$ and $M(g)$ are the molecular weights of the liquid and the gas.

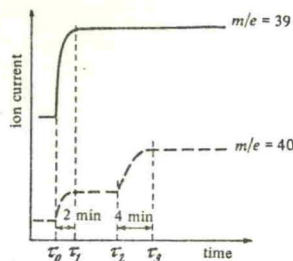


Figure 3. Kinetics of the change of intensity of the mass-spectral lines (argon in toluene experiment)

Fig. 3 shows a typical kinetic plot of the mass-spectral line intensities obtained in the present apparatus. As a concrete example, the experiment on the solubility of argon in toluene is shown. The full line labelled $m/e = 39$ corresponds to the liquid, the broken line ($m/e = 40$) to the gas. The argon is admitted from the gas cylinder to the vessel containing toluene at time τ_0 . This increases the pressure difference across the capillary inlet system, and causes an increase in the intensity of both the $m/e = 39$ (toluene) line and the $m/e = 40$ line, also present in the toluene mass spectrum. The diffusion time of the argon molecules to the inlet split is very large on the present scale, and therefore the intensity ratio of the $m/e = 39$ and $m/e = 40$ lines is characteristic of pure toluene and does not indicate the presence of argon. The electromagnetic stirrer was switched on at time τ_2 : the intensity of the $m/e = 39$ toluene line was unaffected, but that of the $m/e = 40$ line began to increase as the gas dissolved in the liquid. At time τ_3 equilibrium was achieved and the solution became saturated.

Fig. 4 shows the measured solubilities of argon in benzene and in toluene as a function of argon pressure. The mole fraction of argon in the solution is plotted vertically. The measurements were made on different days, and the temperature was $20 \pm 1^\circ\text{C}$ for benzene and $17.3 \pm 0.2^\circ\text{C}$ for toluene. The liquids were of "analytically pure" grade, the argon contained 0.1% N_2 and 0.01% O_2 impurities. The experiments confirm that Henry's law applies to the present solutions (mean scatter of the points from the straight lines $\pm 3\%$). The solubility at 1 atm is numerically

† Since the mass spectra of the gas and the liquid are superimposed, a correction must be applied for any contribution of the liquid to lines characteristic of the gas.

equal to the slope of the experimental straight lines. These results are consistent with those of previous workers (with the exception of Eremina¹²) within experimental error:

Mixture	$10^4 N_{\text{Ar}}$, mole fraction Ar	
	this work	published data
Argon-benzene	8.44 ± 0.25	7.94 ± 0.08 (Ref.12)
		8.73 ± 0.18 (Ref.13)
		8.77 ± 0.20 (Ref.14)
Argon-toluene	10.42 ± 0.31	9.41 ± 0.09 (Ref.12)
		10.74 ± 0.21 (Ref.13)
		10.897 ± 0.015 (Ref.15)

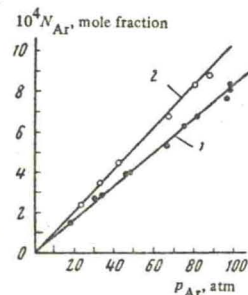


Figure 4. Solubility of argon as a function of gas pressure in 1) benzene and 2) toluene

The slight disagreement with published data may be ascribed to systematic error in the methods used by the previous workers¹²⁻¹⁵, since our procedure appears to exclude the possibility of systematic errors from uncontrolled loss of material during sampling.

Thus, the method described offers new possible applications of the mass spectrometer in thermodynamic and kinetic studies of liquids, arising from the choice of a capillary liquid inlet system.

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