SHORTER CONTRIBUTION

Co-distillation of boric acid with water under ambient conditions

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Many studies of the co-distillation of boric acid with water have been reported in the literature, one of the most comprehensive being that of Stackelberg et al. (1937), who calculated a partial pressure for boric acid at 109° of 0.62 mm. This is considerably less than had been found by earlier workers, and Stackelberg argued convincingly that the early high values resulted from poor experimental design. He also showed that Henry's Law is valid for the system $H_2O/B(OH)_3$.

The presence of high boron/chlorinity ratios in rain water compared to those in sea water has been couched in terms of this co-distillation phenomenon (Gast & Thompson, 1958; Bruyevich & Korzh, 1971). Gast & Thompson demonstrated in a laboratory experiment that condensate collected at 12° from a 32° air stream that had been blown gently over a 25° 3.249 mg B/l boric acid solution contained as much 60 μg B/l. Henry's Law calculations based on the data presented by Stackelberg et al. indicate a concentration of boron of approximately 2.7 μg/l is to be expected in distillate from a 3.2 mg/l B solution at 109°. This suggests that the boron concentration in the condensate of Gast and Thompson's experiment was much higher than in the vapor stream prior to condensation, implying that further fractionation had taken place during the condensation step itself. The much lower value (0.42 μg/l) obtained by Nishimura & Tanaka (1972) for condensate in the same experiment, but using a dry-ice condensation temperature, would seem to confirm this conclusion. The reason for the discrepancy between the two reported values becomes clear below.

Certain results of ours obtained during a study of cooling tower "drift loss" using boron as a trace element also led us to suspect that fractionation caused Gast & Thompson's values to be too high. A brief mass-balance analysis on the condensation of a boron-containing vapor stream was therefore carried out as follows.

For boron, assuming that its mole fractions in the original solution and in the condensate remain effectively constant during the experiment, from Fig. 1

$$X_F Q_F = X_C \frac{dV_c}{dt} + X_D\left(Q_F - \frac{dV_c}{dt}\right)$$

If $100R$ = percent recovery where

$$R = \frac{dV_c}{dt} \Big/ Q_F$$

then

$$\frac{X_F}{R} = X_C + X_D\left(\frac{1}{R} - 1\right)$$

or

$$X_C = \frac{1}{R}(X_F - X_D) + X_D \qquad \text{(i)}$$

The partial pressure of boric acid in stream D is PX_C, and of water in stream D is approximately P' where P, P' are vapor pressures of boric acid and water at T_C respectively.

Therefore

$$\frac{X_D}{X_H} = \frac{PX_C}{P'} \quad \text{or} \quad X_D \simeq \frac{PX_C}{P'} \qquad \text{(ii)}$$

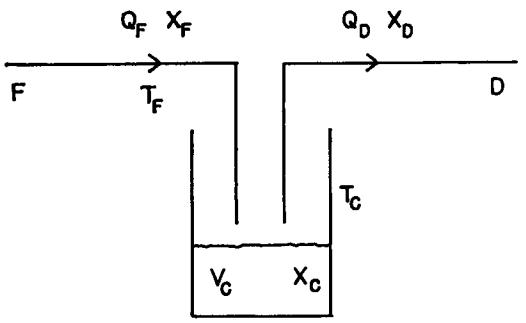

Fig. 1. Condensation Stage. Q_F, X_F, T_F, are rate of flow, boron mole fraction and temperature, respectively, of feed stream F. Similarly Q_D and X_D are rate of flow and boron mole fraction of departing stream D. V_C and X_C are volume and boron mole fraction of condensate. $T_F > T_C$.

(where X_H is the mole fraction of water in the departing stream D).

It follows from (i) and (ii) that

$$X_C = \frac{1}{R}\left(X_F - \frac{PX_C}{P'}\right) + \frac{PX_C}{P'}$$

or

$$X_C = X_F \Big/ \left(R + \frac{P}{P'} - \frac{RP}{P'}\right)$$

At

$$R = 1,\ X_C = X_F$$

As

$$R \to 0,\ X_C \to X_F \frac{P'}{P}$$

Since P'/P is always $\geqslant 1$ X_C must always be greater than X_F for recoveries of less than 100%. It is unlikely for instance, that full recovery of a 32° vapor stream is possible in a simple condenser at 12°, which is consistent with the high concentrations of boron found in condensate by Gast & Thompson. Nishimura & Tanaka using a similar apparatus, but with condensation at −78.5°C, probably achieved close to 100% recovery, resulting in their much lower value.

The cooling tower drift loss determination (Matson et al., 1973) will be reported in detail elsewhere. In summary, by following the rate of change of concentration of a trace substance in a cooling system during a period of no "blowdown", and knowing the evaporative loss rate in the cooling tower during that period, the drift loss, or loss by droplet spray, of cooling water from the tower may be calculated. If the total amount of cooling water in the system is maintained constant by make up, any decrease in tracer concentration must occur as a result of drift loss alone, assuming that the tracer material is suitably involatile. Initially, boric acid was used as a tracer. At a later date under essentially the same conditions, the experiment was repeated with chromate as the trace material. Identical results were obtained for each determination, which would not have been expected if, during the evaporation of 1 l of water, 60 μg or more of boric acid also evaporated.

Distillation is undoubtedly important as a mechanism for the introduction of boron into the atmosphere. The above discussion indicates, however, that the fractional nature of this distillation should be taken into account in interpreting experimental results or high concentrations measured in atmospheric water bodies and rainwater.

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