

Thermodynamics of aqueous H₂S solutions at elevated temperatures: Solubility and first dissociation constant

R.E. Krupp

Bundesanstalt für Geowissenschaften und Rohstoffe, Postfach 51
01 53, D-30631 Hannover, Germany.

O.M. Suleimenov

Institut für Mineralogie und Petrographie, ETH-Zentrum,
CH-8092 Zürich, Switzerland.

The solubility of hydrogen sulphide in pure water and in NaCl solutions has been studied experimentally from 20 to 320°C and at saturation pressures. Hydrogen sulphide solutions in equilibrium with their vapor phase were contained in a pressurized titanium bellows of known total volume. The bellows transmitted inside-vapor pressures via a thermally stable oil (pressure medium) to a high-precision pressure sensor. Temperatures were measured by a sheathed thermocouple immersed into the oil surrounding the bellows. Values for the Henry constants were derived from measurements of equilibrium vapor pressure, volume, temperature, and bulk composition.

The Henry constants agree well with previously published data up to about 200°C, but then deviate towards lower values (higher solubilities) at higher temperatures. Henry constants from 20 to 320°C and at saturation pressures may be obtained from the correlation

$$\log K_H(T, P_{\text{sat},1}) = + 0.6342702616e+3 \\ + 0.2709284796e+0 \cdot T - 0.1113202904e-3 \cdot T^2 \\ - 0.1671907660e+5/T - 0.2619219571e+3 \cdot \log T,$$

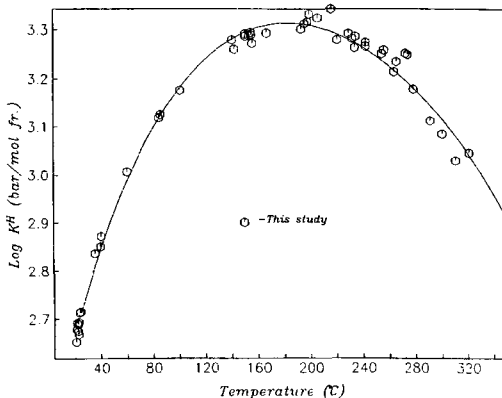


FIG. 1. Scaled particle theory model fitted to the experimental Henry constants determined in this study.

where K_H is in units of bar/molality and T in Kelvin.

The experimental Henry constants have been fitted to a scaled particle theory model (Fig. 1) and have been tested by a linearization procedure proposed by Japas and Levelt-Sengers (1989).

The salting-out effect of NaCl on H₂S solubility is nearly independent of temperature up to about 250°C, but then increases sharply as temperatures approach the critical point of water (Fig. 2).

Skeleton tables to 365°C and for ionic strengths $\mu = 0, 1, 2, 3$ have been prepared.

Attempts to determine the first dissociation constant, pK_1 , of H₂S by evaluating H₂S partial pressures as a function of the degree of neutralization yielded results with extremely large uncertainties. The difficulties arose from the fact

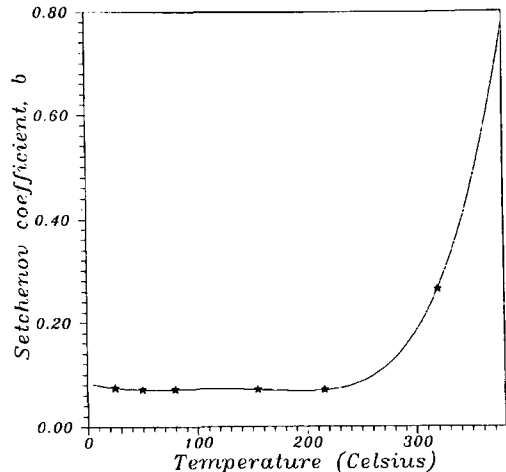


FIG. 2. Temperature dependence of the salting-out effect on H₂S illustrated by the Setchenov coefficients at various temperatures. Data from Barrett *et al.* (1988), Gamsjäger and Schindler (1969), and this study.

that both, pH and pK_1 had to be calculated from the measured vapor pressure, composition and volume data.

An improvement was achieved by measuring the H_2S vapour pressure of phosphate buffer solutions. For this purpose some modifications of the equipment were necessary in order to cope with corrosion of titanium by phosphate ions at high temperatures. First results indicate pK_1 values for H_2S close to those predicted by Barbero *et al.* (1982). However, further measurements are required before reliable extrapolations to infinite dilution will be possible.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft, grants Kr763/6-1,2 is gratefully acknowledged.

References

- Barbero J.A., McCurdy K.G. and Tremaine P.R. (1982) *Can. J. Chem.*, **60**, 1872–80.
- Barrett T.J., Anderson G.M. and Lugowski J. (1988) *Geochim. Cosmochim. Acta*, **52**, 807–11.
- Gamsjäger H. and Schindler P. (1969) *Helv. Chim. Acta*, **52**, 1395–402.
- Japas M.L. and Levelt-Sengers J.M.H. (1989) *Amer. Inst. Chem. Eng. J.*, **35**, 705–13.