Phase Relations for H₂S-H₂O System. The lower thermodynamically stable temperature limit of safe operation is that at which formation of ice-like crystals of H₂S hydrate occurs. A phase diagram of the H_2S-H_2O system is shown in Figure 1. The indicated phase diagram and the corresponding lower limit of the cold tower temperature are applicable only for the system pure H_2S-H_2O , and it would be possible in principle to lower the limit for the dual temperature process advantageous by adding a third component.

Relative Thermal Capacity of Gas and Liquid Streams, γ . The values of γ , the relative thermal capacity at selected temperatures and flow rates of the gas and liquid streams, were calculated from data in Table II. They are plotted in Figure 5 and shown in Table VI.

Potential Energy of Liquid and Gas Streams. The potential energy of a stream is equal to its weight times its elevation.

 $(P.E.)_{G} = (34.08 + 18.016h)(1.5)(z)(1/1400), p.c.u./pound-mole H_2S$

where 34.08 and 18.016 are the molecular weights of H₂S and H_2O , 1.5 feet are the tray spacing, z, the number of trays, and 1400 foot-pounds equals 1 p.c.u. The value of the humidity, h, varies from 0.0034 at 30° C. and 250 p.s.i.a. to 0.0058 at 40° C. and 244 p.s.i.a. Using an average value of h:

$$(P.E.)_{G} = 0.0366 z, p.c.u. / pound-mole H_2S$$

and

$$\frac{d(P.E.)_G}{dz} = 0.0366 \text{ p.c.u.} / (\text{pound-mole } H_2S)(\text{tray})$$

Variation of h over the range given would result in only 0.1% change in (P.E.)₆, and variation of S would result in 1.0% change in (P.E.)_L. Similarly

 $(P.E.)_L = (18.016 + 34.08S)(1.5)(z)(1/1400), p.c.u./pound-mole H_2O.$

S varies from 0.0197 at 40° C. and 244 p.s.i.a. to 0.0253 at 30° C. and 250 p.s.i.a. Using an average value of S:

 $(P.E.)_L = 0.0201 z, p.c.u. / pound-mole H_2O$

and

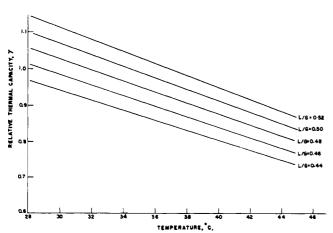


Figure 5. Variation of relative thermal capacity $\gamma = LC_L/GC_G$ with temperature and relative flow for countercurrent H₂S gas and H₂S at saturation equilibrium and at 250 p.s.i.a.

CORRECTION

In "Heat Transfer Characteristics of Fluorochemical Inert Liquid FC-75" [M.C. Marcellus, A.F. Spilhaus, Jr., and L.A. Troeltzsch, J. CHEM. ENG. DATA 6, 459 (1961),

$$\frac{d(\mathbf{P}.\mathbf{E}.)_L}{dz} = 0.0201, \text{ p.c.u.} / (\text{pound-mole } H_2 \text{O}) (\text{tray})$$

For a 6-p.s.i. drop across 70 trays:

$$\frac{dp}{dz} = \frac{-6}{70} = -0.08571 \text{ p.s.i./tray}$$

Heat of Reaction for Isotope Excannge Reaction. The heat of the exchange can be estimated from the results of Suess (7). From these results, it can be calculated that the experimental determination of the equilibrium at elevated temperatures (350° to 500° C.) fits the heat of exchange shown:

 $H_2O(g) + D_2S(g) = D_2O(g) + H_2S(g); \Delta H_e^0 = -733 \text{ cal./mole } D$

$$K_{g} = \frac{[D_{2}O]_{g}}{[D_{2}S]_{g}} \frac{[H_{2}S]_{g}}{[H_{2}O]_{g}} = 0.662e^{1466/RT_{h}}$$

Theoretical calculations made by Geib and Suess indicate for reactions in the temperature range 0° to 100° C.:

 $H_2O(g) + HDS(g) = HDO(g) + H_2S(g); \Delta H_e^0 = -463 \text{ cal./mole } D$

$$K_{g} = 1.010e^{463/RT_{k}} = \frac{[\text{HDO}]_{g} [\text{H}_{2}\text{S}]_{g}}{[\text{H}_{2}\text{O}]_{g} [\text{HDS}]_{g}}$$

 $H_2O(l) + HDS(g) = HDO(l) + H_2S(g); \Delta H_e^0 = -593 \text{ cal./mole } D$

$$K_{L} = 0.871 e^{593/RT_{k}} = \frac{[\text{HDO}]_{l} [\text{H}_{2}\text{S}]_{g}}{[\text{H}_{2}\text{O}]_{l} [\text{HDS}]_{g}}$$

From these data the theoretical value $\Delta H_e^0 = -593$ cal./mole HDO would apply to the case where liquid water is contacted with gaseous H_2S .

LITERATURE CITED

- (1)Evans, W.H., Wagman, D.D., J. Research Natl. Bur. Standards 49, 141 (1952).
- Hull, H.L., Pohl, H.A., "Thermal Behavior of Countercurrent Equipment," E.I. du Pont de Nemours & Co., Wilmington, (2)Del., U.S. Atomic Energy Comm., Research and Develop. Rept. DP-97, 1954, declassified March 15, 1957.
- Keenan, J.H., Kayes, F.G., "Thermodynamic Properties of Steam," Wiley, New York, 1936. (3)
- (4)
- Kelley, K.K., U.S. Bur. Mines Bull. 406. Lange, N.A., "Handbook of Chemistry," 7th ed., Handbook (5) Publ., Sandusky, Ohio.
- Selleck, F.T., Carmichael, L.T., Sage, B.H., Ind. Eng. Chem. (6)44. 2219 (1952).
- Suess, A.E., FIAT Rev. Ger. Sci., Physical Chemistry (1939-(7)1946), pp. 22-3, U. S. Dept. Commerce, Office Tech. Services, Physical Chemistry, P.B. Rept. 95682, 1948.
- (8)West, J.R., Chem. Eng. Progr. 44, No. 4, 289 (1948).

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the first column of the table on page 460 was misaligned horizontally and should be moved down one line, so that specific gravity is aligned with 1.77, 0.97, and 0.887.