Thermodynamics of the Hydrogen Sulfide–Water System Relevant to the Dual Temperature Process for the Production of Heavy Water

HERBERT A. POHL[1]
Explosives Department, Atomic Energy Division, E.I. du Pont de Nemours & Co., Inc.,Wilmington, Del.

THE DUAL temperature isotope exchange process for heavy water makes use of the variation in hydrogen isotope distribution with temperature of the H_2S-H_2O system. It depends upon the shift in equilibrium of the isotope exchange reaction:

$$H_2O(l) + HDS(g) = HDO(l) + H_2S(g);$$

$$\Delta H_e^0 = -593 \text{ cal./gram atom D (theor.)}$$

The wider the operating temperature interval, the greater the change in isotopic composition of the paired hot and cold towers, and the greater the yield of the process. The practical, upper operating temperature limit is set by economic factors at about 140° C. The lower operating temperature limit is set by the temperature of formation of an ice-like H_2S hydrate (27.4° C. at 250 p.s.i.a.; 28.8° C. at 300 p.s.i.a., Figure 1).

In the case of countercurrent processes where the enthalpies of the two streams are nearly equal, unusual plate-to-plate temperature changes may occur within the system (*2*). For this reason the following detailed analysis has been made of relevant thermodynamic data for the H_2S-H_2O system. In the countercurrent dual-temperature process such normally small enthalpy effects as the nonideality of H_2S gas (Joule-Thompson cooling) and the above reaction play major roles.

DISCUSSION

Thermodynamic Properties of Gaseous and Aqueous H_2S. ENTHALPY OF WET H_2S. The enthalpy of H_2S saturated with water vapor is dependent on temperature and pressure. Changes in enthalpy are evaluated as the gas proceeds from one set of conditions to another in the towers.

ΔH_G = enthalpy to bring 1 mole of pure H_2S gas from 25° C. to T, plus enthalpy change in compressing it from 1 atm. to p, plus enthalpy change in raising h moles of $H_2O(l)$ to T from 25° C., plus enthalpy change of raising h moles of $H_2O(l)$ from the pressure of its own vapor at 25° C. to the pressure of its vapor at temperature T, plus heat of vaporization of h moles of H_2O at T and p.

$$\Delta H_G = C_g(T-25) + \int_{p=1\text{ atm.}}^{p=p} \left(\frac{\partial H_g}{\partial p}\right)_T dp + C_w \times h(T-25) + h\int_{p_0'}^{p'} \left(\frac{\partial H_w}{\partial p}\right)_T dp' + h \times \Delta H_v$$

where

C_g = mean molar heat capacity of pure $H_2S(g)$ in interval 25° C. to T
C_w = mean molar heat capacity of $H_2O(l)$ in interval 25° C. to T
ΔH_v = molar heat of vaporization of H_2O at temperature T
T = vapor temperature, ° C.
h = humidity of H_2S = mole H_2O per mole H_2S

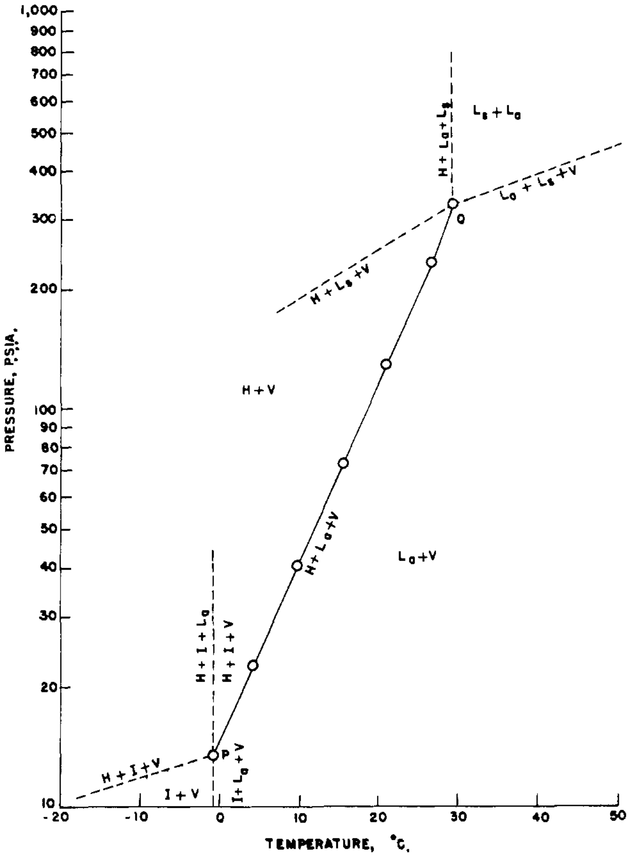

Figure 1. Phase diagram for H_2S–H_2O system

H_g = enthalpy per mole of pure H_2S gas
(different from H_G = enthalpy per mole of H_2S containing moisture)
H_w = enthalpy of liquid water

For present calculations there is needed $[\partial H_G/\partial T]_p$ and $[\partial H_G/\partial p]_T$. Since, in the region of interest, C_w and $(\partial H_g/\partial p)_T$ as shown later are essentially independent of T and p, and C_g and ΔH_v are essentially independent of p while $(\partial H_w/\partial p)_T$ is small and negligible for present purposes,

$$\Delta H_G = C_g(T-25) + \left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_w \times h(T-25) + h \times \Delta H_v$$

and

$$C_G = \left[\frac{\partial H_G}{\partial T_k}\right]_p = C_g + \left(\frac{\partial C_g}{\partial T_k}\right)_p (T-25) + C_w \times h + C_w(T-25)\left(\frac{\partial h}{\partial T_k}\right)_p + \Delta H_v\left(\frac{\partial h}{\partial T_k}\right)_p + h\left(\frac{\partial(\Delta H_v)}{\partial T_k}\right)_p$$

where

C_G = the heat capacity of the wet H_2S
T_k = temperature, ° K.

---

[1] Present address, Plastic Laboratory, Princeton University, Princeton, N. J.

$$\left[\frac{\partial H_G}{\partial p}\right]_T = \left(\frac{\partial H_g}{\partial p}\right)_T + C_w(T - 25)\left(\frac{\partial h}{\partial p}\right)_T + \Delta H_v\left(\frac{\partial h}{\partial p}\right)_T$$

Heat Capacity of H_2S, C_g. For $H_2S(g)$

$$C_p = 7.15 + 3.32 \times 10^{-3}\ T_k$$

[from data of P.C. Cross as given by Kelly (*4*)]

This equation gives C_p at 25° C. as 8.14 cal. per mole deg. However, a recent paper by Evans and Wagman (*1*) reports what are probably more precise values: $C_p = 8.19$ at 25° C.; $C_p = 8.20$ at 27° C.; and 8.53 at 127° C. Accordingly, the relation

$$C_p = 7.20 + 3.32 \times 10^{-3}\ T_k$$

will be used. Since C_g is the mean molar heat capacity of $H_2S(g)$, in the interval T to 25° C.

$$C_g = \frac{C_{p\ 25^\circ\mathrm{C.}} + C_{p,\ T}}{2} = 8.19 + 1.66 \times 10^{-3}\ (T - 25^\circ\ \mathrm{C.})$$

Heat Capacity of Water, C_w. The heat capacity of water is observed to be essentially constant over the interval 25° to 40° C. and equal to 0.9975 cal. per deg. (15° cal.) (5). The molar heat capacity of H_2O is accordingly,

$$C_w = 0.9975 \times 18.016 = 17.971\ \mathrm{cal./mole\ deg.}$$

Heat of Vaporization of Water, ΔH_v. ΔH_v is the heat of vaporization of liquid water into saturated vapor at the temperature specified, T, and at the total pressure equal to the vapor pressure of the liquid. The heat of vaporization varies slightly with the total pressure on the liquid by the amount of change of the PV term in the expression $\Delta H = \Delta E + \Delta(PV)$. Over the pressure range employed (1 to 250 p.s.i.), this amounts to some 6 cal. per mole in the 10,000 cal. per mole ΔH_v; hence its inclusion was omitted as being beyond the precision of present calculations. The heat of vaporization of water varies linearly with temperature throughout the range 25° to 43° C. to within the accuracy of the values shown in Keenan's steam tables (*3*). The expression $\Delta H_v = 10{,}500 + 10.0\ (25 - T)$ (cal. per mole) represents the experimental values with a precision of 2 parts in 10,000 over the range.

Humidity of Gaseous H_2S *Saturated with Water Vapor, h.* Values of gas humidity are calculated from the behavior of H_2S gas and water vapor as determined by Selleck, Carmichael, and Sage (*6*). An analysis of the data of Selleck and others showed that the data on humidity could be represented to within experimental error analytically by the function,

$$\log h = \frac{-2123}{T_k} + 4.53693, \text{ at 250 p.s.i.a.,}$$

and that these values of h multiplied by 1.0155 give the humidity at 244 p.s.i.a. over the temperature range 30° to 43° C. Over the range 250 ± 20 p.s.i., the relation

$$h = \left(\frac{638.1 - p}{75.8}\right) \times 10^{-3} = h_{(250)} + \left(\frac{250 - p}{75.8}\right) \times 10^{-3}\ \frac{\mathrm{mole\ H_2O}}{\mathrm{mole\ H_2S}}$$

describes the changes of h with p to within 0.8%, hence

$$\frac{\partial h}{\partial p} = -\ \frac{10^{-3}}{75.8}\ \frac{\mathrm{mole\ H_2O\ per\ mole\ H_2S}}{\mathrm{p.s.i.}},$$

and

$$h_{T,\ p} = 3.298 \times 10^{-3} - (p)\ \frac{10^{-3}}{75.8} + 10^{(-2123/T_k + 4.53693)}$$

in the prescribed range. Data used to obtain this relation (*6*) are given in Table I.

Change of Enthalpy of Wet, Gaseous H_2S *with Temperature.* The rate of change of enthalpy of wet, gaseous H_2S with temperature, or in other words the effective molar heat capacity, $[\partial H_G/\partial T_k]_p$ of the gas is given, as shown earlier, by

$$C_G = \left[\frac{\partial H_G}{\partial T_k}\right]_p = C_g + (T - 25)\left[\left(\frac{\partial C_g}{\partial T_k}\right)_p + C_w\left(\frac{\partial h}{\partial T_k}\right)_p\right]$$

$$h\left[C_w + \left(\frac{\partial(\Delta H_v)}{\partial T_k}\right)_p\right] + \Delta H_v\left(\frac{\partial h}{\partial T_k}\right)_p$$

Since

$$C_g = 8.19 + 1.66 \times 10^{-3}\ (T - 25),\ \mathrm{cal./deg.\ mole\ H_2S}$$

$$\left(\frac{\partial C_g}{\partial T_k}\right)_p = 1.66 \times 10^{-3}\ \mathrm{cal./mole\ deg.^2}$$

and

$$C_w = 17.971\ \mathrm{cal./deg.\ mole\ H_2O}$$

$$h = 3.298 \times 10^{-3} - p\ \frac{10^{-3}}{75.8} + 10^{-2123/T_k + 4.53693}\ \mathrm{mole\ H_2O/mole\ H_2S}$$

$$\left(\frac{\partial h}{\partial T_k}\right)_p = \frac{4889}{T_k^2} \times 10^{-2123/T_k + 4.53693}\ \frac{\mathrm{mole\ H_2O}}{(\mathrm{mole\ H_2S})(\mathrm{deg.})}$$

$$= \frac{4889}{T_k^2} \times h_{(250\ p.s.i.)}$$

$$\left(\frac{\partial h}{\partial p}\right)_T = -\ \frac{10^{-3}}{75.8}\ \frac{\mathrm{mole\ H_2O}}{(\mathrm{mole\ H_2S})(\mathrm{p.s.i.})}$$

$$\Delta H_v = 10{,}500 + 10.0\ (25 - T)\ \mathrm{cal./mole\ H_2O}$$

$$\left[\frac{\partial(\Delta H_v)}{\partial T_k}\right]_p = -10.0\ \frac{\mathrm{cal.}}{(\mathrm{mole\ H_2O})(\mathrm{deg.})}$$

then

$$\left[\frac{\partial H_G}{\partial T_k}\right]_p = 8.19 + (T - 25)\left[0.00332 + 17.971 \times \frac{4889}{T_k^2} \times 10^{-2123/T_k + 4.53693}\right]$$

$$+ \left[3.298 \times 10^{-3} - p\ \frac{10^{-3}}{75.8} + 10^{-2123/T_k + 4.53693}\right] \times \left[17.971 - 10.0\right] + \left[10{,}500 + 10.0\ (25 - T)\right]$$

$$\times \frac{4889}{T_k^2} \times 10^{-2123/T_k + 4.53693}$$

in

$$\frac{\mathrm{cal.}}{(\mathrm{mole\ H_2S})(\mathrm{deg.})}$$

or

$$\left[\frac{\partial H_G}{\partial T_k}\right]_p = 8.19 + (T - 25)\left[0.00332 + \frac{87{,}860}{T_k^2} \times h_{(250)}\right]$$

$$+ h\,(7.971) + (10{,}750 - 10.0\ T) \times \frac{4889}{T_k^2} \times h_{(250)}$$

Values are given in Table II.

Table I. Humidity of Wet H_2S

Temp., °C.	Temp., °K.	Pressure, P.S.I.A.	Humidity, h, Mole H_2O/Mole H_2S
37.8	310.9	100	0.01071
		200	0.00602
		244	0.00520 (interpolated)
		250	0.00512
		300	0.00462
71.1	344.2	100	0.05340
		200	0.02817
		250	0.02343
		244	0.0238 (interpolated)
		300	0.02030

Change of Enthalpy of Wet, Gaseous H_2S *with Pressure.* The rate of change of enthalpy of wet, gaseous H_2S with pressure is given by:

$$\left[\frac{\partial H_G}{\partial p}\right]_T = \left(\frac{\partial H_g}{\partial p}\right)_T + C_w\,(T-25)\left(\frac{\partial h}{\partial p}\right)_T + \Delta H_v\left(\frac{\partial h}{\partial p}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_T = -\frac{10^{-3}}{75.8}\,\frac{\text{mole } H_2O}{(\text{mole } H_2S)(\text{p.s.i.})}$$

$$\left[\frac{\partial H_g}{\partial p}\right]_T = \text{Joule-Thompson expansion cooling of } H_2S$$

Hydrogen sulfide gas has a large Joule-Thompson coefficient, and cools considerably when expanded, at least at temperatures above 25° C. and pressures above 1 atm., as judged from the calculations of West (*8*). Selected values from West's tables were used to construct Table III which shows the variation of enthalpy with temperature and pressure. From these data, it was concluded that the change of enthalpy with pressure was constant over the pressure and temperature range of 15 to 300 p.s.i.a. and 25° to 50° C.—i.e., $[\partial H_g/\partial p]_T = -1.051$ cal. per mole p.s.i. For a 6.0-p.s.i. pressure drop at about 38° C., the enthalpy change per mole is therefore $\Delta H = -6(-1.051) = +6.306$ cal. per mole at 37.78° C. The value of the coefficient $\Delta H/\Delta p$, for H_2S, by way of comparison, is about 10 times that for air, the latter having a value of -0.121 cal. per mole p.s.i.

Substitution of these values into the equation for the enthalpy change of wet gaseous H_2S with pressure gives:

$$\left[\frac{\partial H_G}{\partial p}\right]_T = -1.051 + 17.971\,(T-25)\left(\frac{-10^{-3}}{75.8}\right)$$

$$+\,[10{,}500 + 10.0(25-T)]\left(\frac{-10^{-3}}{75.8}\right)$$

$$= -1.1870 - 1.052\times10^{-4}\,T,\ \frac{\text{cal.}}{(\text{mole } H_2S)(\text{p.s.i.})}$$

Table III. Change of Enthalpy of Dry, Gaseous H_2S with Pressure

Temp., °F.	Temp., °C.	Pressure, P.S.I.	Pressure, Atm.	Enthalpy, B.t.u. per lb.	Enthalpy, Cal. per mole
80	26.67	14.7	1.0	273.7	5182.5
80	26.67	147	10.0	265.5	5027.2
80	26.67	294	20.0	...	...
100	37.78	14.7	1.0	277.7	5258.2
100	37.78	147	10.0	270.3	5118.1
100	37.78	294	20.0	262.2	4964.7
120	48.89	14.7	1.0	282.5	5349.1
120	48.89	147	10.0	275.5	5216.6
120	48.89	294	20.0	267.7	5068.9

Table II. Solubility, Humidity, Heat Capacity, and Enthalpy of Aqueous H_2S Solutions and Wet Gaseous H_2O at 250 P.S.I.A.

Temp., ° C.	$h\times10^{3}$ [a]	S [b]	T_k°	$\left(\frac{\partial h}{\partial T}\right)_p \times 10^3$	C_g, [c]	ΔH_v	(C_G), [c] $\left[\frac{\partial H_G}{\partial T_k}\right]_p$ [c]	$\left[\frac{\partial H_G}{\partial p}\right]_T$	$\left(\frac{\partial S}{\partial T_k}\right)_p \times 10^3$	(C_L) [c] $\left[\frac{\partial H_L}{\partial T_k}\right]_p$ [c]	v_w, Ml.	$\left[\frac{\partial v_w}{\partial T_k}\right]_p$, Ml./Degree	$\left[\frac{\partial H_L}{\partial p}\right]_T$	b_L [d]	B_G [d]
30	3.417	0.02534	303.1	0.1818	8.1983	10,450	10.1500	−1.1902	−0.5938	21.6780	1.00421	3.034×10^{-4}	−0.4256	0.05658	0.1386
31	3.603	0.02475	304.1	0.1905	8.2000	10,440	10.2480	−1.1903	−0.5762	21.5487		3.124×10^{-4}	−0.4104	0.05528	0.1386
32	3.798	0.02419	305.1	0.1995	8.2016	10,430	10.3494	−1.1904	−0.5595	21.4259		3.213×10^{-4}	−0.3959	0.05403	0.1386
33	4.002	0.023633	306.1	0.2088	8.2033	10,420	10.4542	−1.1905	−0.5430	21.3055		3.301×10^{-4}	−0.3818	0.05282	0.1386
34	4.215	0.023100	307.1	0.2185	8.2049	10,410	10.5634	−1.1906	−0.5273	21.1914		3.387×10^{-4}	−0.3683	0.05167	0.1386
35	4.439	0.022580	308.1	0.2286	8.2066	10,400	10.6771	−1.1907	−0.5121	21.0811	1.00610	3.473×10^{-4}	−0.3552	0.05054	0.1387
36	4.673	0.022075	309.1	0.2391	8.2083	10,390	10.7953	−1.1908	−0.4975	20.9752		3.557×10^{-4}	−0.3425	0.04946	0.1387
37	4.917	0.021585	310.1	0.2500	8.2099	10,380	10.9179	−1.1909	−0.4834	20.8741		3.640×10^{-4}	−0.3303	0.04841	0.1387
(37.8)	5.121	0.02120	310.9	0.2590	8.2112	...	...	...	...	...		...	...	...	...
38	5.173	0.02112	311.1	0.2613	8.2116	10,370	11.0452	−1.1910	−0.4698	20.7766		3.721×10^{-4}	−0.3186	0.04741	0.1387
39	5.440	0.02065	312.1	0.2730	8.2132	10,360	11.1767	−1.1911	−0.4564	20.6812		3.801×10^{-4}	−0.3071	0.04642	0.1387
40	5.719	0.020195	313.1	0.2852	8.2149	10,350	11.3142	−1.1912	−0.4436	20.5903	1.00768	3.883×10^{-4}	−0.2960	0.04547	0.1387
41	6.010	0.01976	314.1	0.2978	8.2166	10,340	11.4559	−1.1913	−0.4312	20.5025		3.961×10^{-4}	−0.2854	0.04456	0.1387
42	6.315	0.01933	315.1	0.3110	8.2182	10,330	11.6045	−1.1914	−0.4192	20.4179		4.039×10^{-4}	−0.2750	0.04367	0.1387
43	6.632	0.01892	316.1	0.3245	8.2199	10,320	11.7564	−1.1915	−0.4077	20.3371		4.117×10^{-4}	−0.2651	0.04282	0.1387

[a] Mole H_2O/mole H_2S.
[b] Mole H_2S/mole H_2O.
[c] Cal./mole degree.
[d] b_L and B_G are necessary coefficients in the equations given by (*2*) for thermal feedback in countercurrent systems. They are listed here for convenience in later references.

ENTHALPY OF AQUEOUS H_2S SOLUTIONS. The enthalpy of water saturated with H_2S is dependent on temperature and pressure. It is desired to evaluate those changes in enthalpy as the solution proceeds from one set of conditions to another in the towers.

ΔH_L = enthalpy to bring 1 mole of pure H_2O from 25° C. to t, plus enthalpy to bring 1 mole of pure H_2O from its vapor pressure p_0' at 25° C. to p, plus enthalpy change in raising S moles of H_2S from 25° C. to t plus enthalpy change in bring S moles of H_2S at t from 1 atm. to p, plus enthalpy of solution of S moles of H_2S in 1 mole of H_2O at p and t

$$\Delta H_L = C_w(t - 25) + \int_{p_0'}^{p} \left(\frac{\partial H_w}{\partial p}\right)_T dp + S \times C_g(t - 25)$$

$$+ S \times \int_{p = 1\text{ atm.}}^{p} \left(\frac{\partial H_g}{\partial p}\right)_T dp + \int_0^S \Delta H_s \, dS$$

where

S = mole H_2S per mole H_2O = solubility of H_2S in water
ΔH_s = heat of solution in water of 1 mole H_2S at temperature t
C_w = heat capacity of water, mean molar over range 25° C. to t
C_g = heat capacity of H_2S, mean molar over range 25° C. to t
t = liquid temperature, ° C.
H_w = enthalpy of liquid water
H_g = enthalpy of dry gaseous H_2S

Now,

$$dH_L = \left[\frac{\partial H_L}{\partial T_k}\right]_p dt + \left[\frac{\partial H_L}{\partial p}\right]_{T_k} dp$$

By application of the first and second laws of thermodynamics

$$\left(\frac{\partial H_w}{\partial p}\right)_T = v_w - T_k\left(\frac{\partial v_w}{\partial T_k}\right)_p$$

where v_w is the molar volume of liquid water.

Since, in the region of interest, C_w, $(\partial H_g/\partial p)_T$, and $(\partial v_w/\partial T_k)_p$ are essentially independent of temperature and pressure; and C_g, $(\partial H_w/\partial p)_T$, ΔH_s, and v_w are essentially independent of pressure and solubility, we may write

$$\Delta H_L = C_w(t - 25) + \left[v_w - T_k\left(\frac{\partial v_w}{\partial T_k}\right)_p (p - p_0')\right]$$

$$+ S\left[\left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_g(t - 25) + \Delta H_s\right]$$

Hence

$$C_L = \left[\frac{\partial H_L}{\partial T_k}\right]_p = C_w + \frac{\partial S}{\partial T_k}$$

$$\left[\left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_g(t - 25) + \Delta H_s\right]$$

$$+ S\left[C_g + \left(\frac{\partial C_g}{\partial T_k}\right)_p (t - 25) + \left(\frac{\partial(\Delta H_s)}{\partial T_k}\right)_p\right]$$

where

C_L = effective molar heat capacity of the solution

and

$$\left[\frac{\partial H_L}{\partial p}\right]_T = \left[v_w - T_k\left(\frac{\partial v_w}{\partial T_k}\right)_p\right] + \frac{\partial S}{\partial p}$$

$$\left[\left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_g(t - 25) + \Delta H_s\right] + \left(\frac{\partial H_g}{\partial p}\right)_T S$$

The Heat of Solution of H_2S, ΔH_s. Examination of the data of Wright and Maass as summarized by Kelley (4) permitted an evalution of the heat of solution of H_2S in water. In this connection, the Van't Hoff equation is useful:

$$\frac{d(\ln c)}{dT_k} = \frac{\Delta H_s}{RT_k^2} \qquad \text{or} \qquad \frac{d(R \ln c)}{d(1/T_k)} = \Delta H_s$$

where c is the observed solubility at 1 atm.

Table IV gives the data of Wright and Maass. Table V gives data derived here from the data of Selleck, Carmichael, and Sage (6).

The values of the heat of solution obtained from both sources are plotted in Figure 2. The values of ΔH_s can be well described over the 5° to 80° C. range by the equation:

$$\Delta H_s = -5182.5 + 39.5\, t^\circ \text{ C.}$$

and by this calculation would have the values −4005 and −3612.5 cal. per mole at 30° and 40° C., respectively. A numerically decreasing heat of solvation of the H_2S molecule is indicated. It would appear that the formation of the $H_2S\text{-}(H_2O)_x$ complex is favored by lower temperatures.

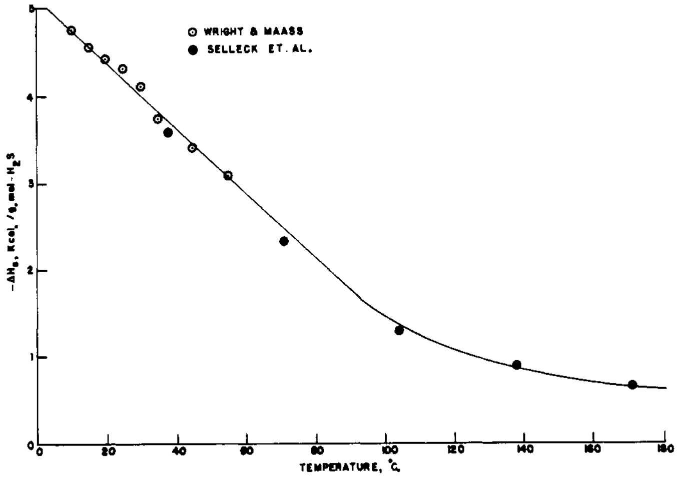

Figure 2. Heat of solution of H_2S in water

Solubility of H_2S *in Water, S*. A survey of the literature on the solubility of H_2S in water showed the determinations of Selleck, Carmichael, and Sage (6) to cover the range of pressures and temperatures required here. Their data in these ranges are summarized in Figure 3 and 4. Their data may be presented analytically to within experimental error over the temperature range 25° to 70° C. at 250 p.s.i.a. by the equation

$$\log S = \frac{935.00}{T_k} - 4.6810$$

and more broadly by

$$\log S = \frac{935.00}{T_k} - 7.07894 + \log p$$

over the pressure range 200 to 350 p.s.i.a., where

S = solubility of H_2S, mole H_2S/mole H_2O
T_k = absolute temperature, ° K.
p = total system pressure, p.s.i.a.

(The expression $\log S = 935.00/T_k - 7.07729 + \log p_1$, where p_1 is the partial pressure of the H_2S, is applicable over a range from about 1 to 350 p.s.i.a., but is somewhat less convenient for present purposes.)

Change of Enthalpy with Temperature of Water Containing Dissolved H_2S. The rate of change of enthalpy with tem-

Table IV. Heat of Solution of H_2S in Water (Wright and Maass Data)

t, ° C.	T, ° K.	$1/T_k \times 10^3$	$-R \ln c$	$\Delta(R \ln c)$ from T to $T + 10°$ K.	$\Delta(1/T_k)$	$-\Delta H_s \times 10^3$
5	278.1	3.59582	3.429	0.594	0.12481	4.759
10	283.1	3.53232	3.730	0.550	0.12052	4.563
15	288.1	3.47101	4.023	0.514	0.11626	4.421
20	293.1	3.41180	4.280	0.484	0.11256	4.2995
25	298.1	3.35457	4.537	(227, $\Delta T = 5°$)	(0.05533)	(4.10)
30	303.1	3.29924	4.764	0.394	0.10538	3.739
40	313.1	3.19386	5.158	0.338	0.09885	3.419
50	323.1	3.09501	5.496	0.285	0.09291	3.067
60	333.1	3.00210	5.781	...	...	...

Table V. Calculations of Heat of Solution of H_2S in Water (From data of Selleck and others)

Pressure, P.S.I.A.	Temp., ° C.	Water Vapor Pressure, P.S.I.A.	H_2S Partial Pressure, P.S.I.A.	Soly., S, Mole/Mole H_2O	Soly., Mole H_2S/1000 G. $H_2O = 55.52 \cdot S$	c = Soly. at 1 Atm., Mole /1000 G.· H_2O	$-\Delta H_s$ Cal./Mole
250	37.8	0.949	249.05	0.0219	$1.176\underline{5}$	$0.06944\underline{2}$	3580
250	71.1	4.74	245.26	0.1297	$0.720\underline{1}$	$0.04316\underline{0}$	2330
250	104.4	17.188	232.81	$0.00985\underline{6}$	$0.547\underline{2}$	$0.03455\underline{2}$	1280
250	137.8	49.20	200.8	$0.00758\underline{7}$	$0.421\underline{2}$	$0.03083\underline{4}$	880
250	171.1	117.99	132.0	$0.00464\underline{1}$	$0.257\underline{7}$	$0.02869\underline{8}$	670

Table VI. Heat Capacity Ratio and Relative Thermal Capacities of Gaseous H_2S and Liquid H_2O Saturated with Each Other at 250 P.S.I.A.

Temp., ° C.	C_L/C_G	γ at $L/G = 0.52$	γ at $L/G = 0.50$	γ at $L/G = 0.48$	γ at $L/G = 0.46$	γ at $L/G = 0.44$
30	2.13576	1.11060	1.06788	1.02516	0.98245	0.93973
31	2.10272	1.09341	1.05136	1.00931	0.96725	0.92520
32	2.07025	1.07653	1.03513	0.99372	0.95232	0.91091
33	2.03798	1.05975	1.01899	0.97823	0.93747	0.89671
34	2.00611	1.04318	1.00306	0.96293	0.92281	0.88269
35	1.97442	1.02670	0.98721	0.94772	0.90823	0.86874
36	1.94299	1.01035	0.97150	0.93264	0.89378	0.85492
37	1.91191	0.99419	0.95596	0.91772	0.87948	0.84124
38	1.88105	0.97815	0.94053	0.90290	0.86528	0.82766
39	1.85038	0.96220	0.92519	0.88818	0.85117	0.81417
40	1.81986	0.94633	0.90993	0.87353	0.83714	0.80074
41	1.78968	0.93063	0.89484	0.85905	0.82325	0.78746
42	1.75948	0.91493	0.87974	0.84455	0.80936	0.77417
43	1.72987	0.89953	0.86494	0.83034	0.79574	0.76114

perature of water containing dissolved H_2S, or the effective molar heat capacity of the solution, C_L, is given as shown earlier, by

$$C_L = \left[\frac{\partial H_L}{\partial T_k}\right]_p = C_w + \frac{\partial S}{\partial T_k}$$

$$\times \left[\left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_g(t - 25) + \Delta H_s\right]$$

$$+ S\left[C_g + \left(\frac{\partial C_g}{\partial T_k}\right)_p (t - 25) + \left(\frac{\partial(\Delta H_s)}{\partial T_k}\right)_p\right]$$

Since

$$C_g = 8.19 + 1.66 \times 10^{-3}\ (t - 25) \text{ in cal. per deg. mole } H_2S$$

$$\left(\frac{\partial C_g}{\partial T_k}\right)_p = 1.66 \times 10^{-3} \frac{\text{cal.}}{(\text{mole } H_2S)(\text{deg.})}$$

$$C_w = 17.971 \frac{\text{cal.}}{(\text{deg.})(\text{mole } H_2O)}$$

$$\log S = \frac{935.00}{T_k} - 7.07894 + \log p$$

$$S = p \times 10^{935/T_k - 7.07894} \frac{\text{mole } H_2S}{\text{mole } H_2O}$$

$$\left(\frac{\partial S}{\partial T_k}\right)_p = -p \frac{2153}{T_k^2} \times 10^{935/T_k - 7.07894} \frac{\text{mole } H_2S}{(\text{mole } H_2O)(\text{deg.})}$$

$$= -\frac{2153}{T_k^2} S$$

$$\left(\frac{\partial H_g}{\partial p}\right)_T = -1.051 \frac{\text{cal.}}{(\text{mole})(\text{p.s.i.})}$$

$$\Delta H_s = -5182.5 + 39.5\,t \text{ cal./mole } H_2S$$

$$\left(\frac{\partial H_s}{\partial T_k}\right)_p = 39.5 \frac{\text{cal.}}{(\text{mole } H_2S)(\text{deg.})}$$

The known values can be substituted to obtain:

$$\left[\frac{\partial H_L}{\partial T_k}\right]_p = 17.971 - \frac{2153 \cdot S}{T_k^2}$$

$$\times [-1.051\,(p - 14.7) + 8.19\,(t - 25) + 1.66 \times 10^{-3}$$

$$(t - 25)^2 - 5182.5 + 39.5t] + S[8.19 + 1.66 \times 10^{-3}$$

$$(t - 25) + 1.66 \times 10^{-3}(t - 25) + 39.5] = 17.971$$

$$- \frac{2153 \cdot S}{T_k^2} [-5371.8 + 47.69t + 1.66 \times 10^{-3}(t - 25)^2$$

$$- 1.051p] + S[47.61 + 3.32 \times 10^{-3}t]$$

Change of Enthalpy with Pressure of Water Containing Dissolved H_2S. The rate of change of enthalpy with temperature of water containing dissolved H_2S is given, as shown earlier, by

$$\left[\frac{\partial H_L}{\partial p}\right]_T = v_w - T_k\left(\frac{\partial v_w}{\partial T_k}\right)_p$$

$$+ \frac{\partial S}{\partial p}\left[\left(\frac{\partial H_g}{\partial p}\right)_T (p - 14.7) + C_g(t - 25) + \Delta H_s\right] + S\left[\frac{\partial H_g}{\partial p}\right]_T$$

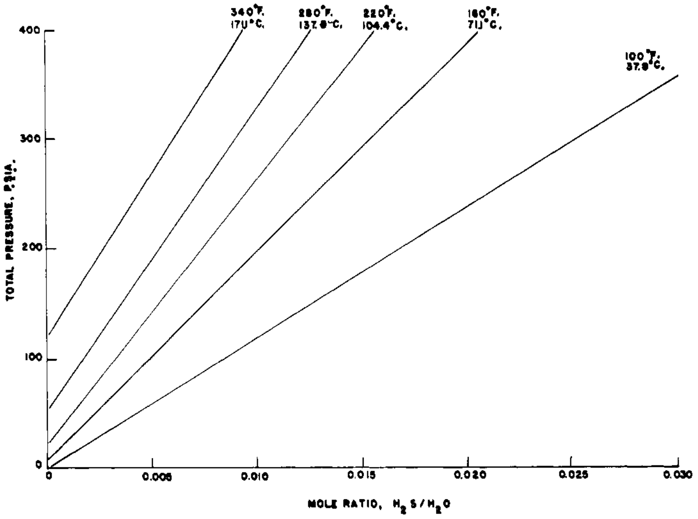

Figure 3. Solubility of H_2S in H_2O

The new term in this expression may be evaluated as follows:

$$v_w = v_0[1 - 5.3255 \times 10^{-5}t + 7.61532 \times 10^{-6}t^2 - 4.37217 \times 10^{-8}t^3 + 1.64322 \times 10^{-10}t^4]$$

over the range 0° to 80° C. (5)

$$v_0 = (0.999841 \text{ g./cc.})^{-1} = 1.0001590 \text{ cc./g.}$$

$$= (18.016 \text{ g./mole}) \times 1.0001590 \text{ cc./g.}$$

$$= 18.019 \text{ cc./mole } H_2O$$

$$v_w = 18.019[1 - 5.3255 \times 10^{-5}t + 7.61532 \times 10^{-6}t^2 - 4.37217 \times 10^{-8}t^3 + 1.64322 \times 10^{-10}t^4] \text{ cc./mole } H_2O$$

$$\left[\frac{\partial v_w}{\partial T_k}\right]_p = 18.019[-5.3255 \times 10^{-5} + 1.523064 \times 10^{-5}t - 1.311651 \times 10^{-7}t^2 + 6.57288 \times 10^{-10}t^3] \text{ cc./(deg.)(mole } H_2O)$$

Conversion of the above volume units to heat units was done by using the gas constant:

$$R = 82.054 \text{ cc. atm. deg.}^{-1} \text{ mole}^{-1} = 1.98647 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$= 82.054 \text{ cc. atm.} \times 14.696 \text{ p.s.i./atm. deg.}^{-1} \text{ mole}^{-1}$$

Hence

$$\frac{1 \text{ cc.}}{\text{mole}} = 1.64733 \times 10^{-3} \frac{\text{cal.}}{\text{p.s.i. mole}}$$

$$v_0 = 18.019 \frac{\text{cc.}}{\text{mole } H_2O} \times 1.64733 \times 10^{-3} \frac{\text{cal.}}{\text{p.s.i. cc.}}$$

$$= 0.029683 \frac{\text{cal.}}{\text{p.s.i. mole } H_2O}$$

and

$$v_w = 0.029683[1 - 5.3255 \times 10^{-5}t + 7.61532 \times 10^{-6}t^2 - 4.37217 \times 10^{-8}t^3 + 1.64322 \times 10^{-10}t^4] \frac{\text{cal.}}{\text{p.s.i. mole } H_2O}$$

and

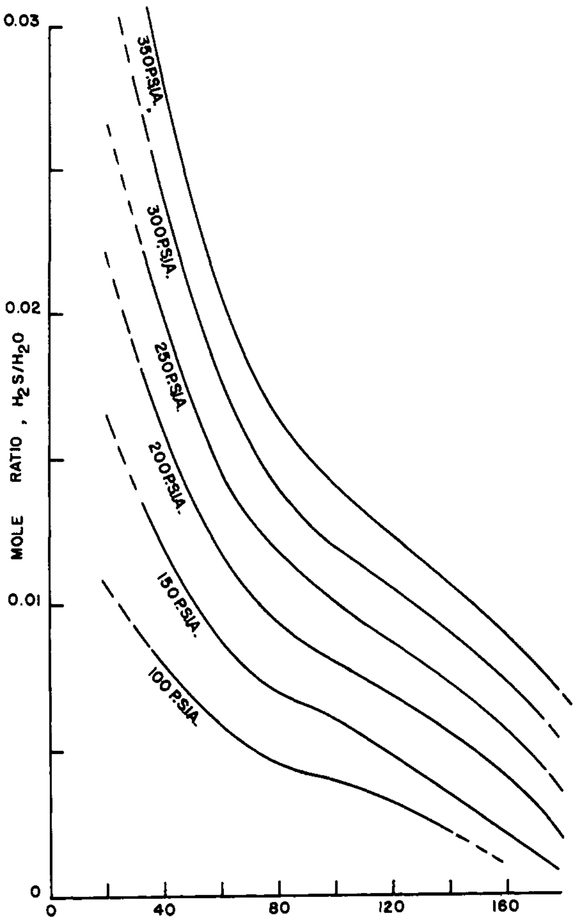

Figure 4. Solubility of H_2S in H_2O

$$\left[\frac{\partial v_w}{\partial T_k}\right]_p = 0.029683[-5.3255 \times 10^{-5} + 1.523064 \times 10^{-5}t - 1.311651 \times 10^{-7}t^2 + 6.57288 \times 10^{-10}t^3] \frac{\text{cal.}}{\text{p.s.i. deg. mole}}$$

$$\frac{\partial S}{\partial p} = 10^{935/T_k - 7.07894} = \frac{S}{p} \quad \frac{\text{mole } H_2S}{(\text{mole } H_2)(\text{p.s.i.})}$$

With these and terms evaluated earlier, the numerical value for the change of enthalpy of the solution with pressure is given as:

$$\left[\frac{\partial H_L}{\partial p}\right]_T = 0.029683\,[1 - 5.3255 \times 10^{-5}t + 7.61532 \times 10^{-6}t^2 - 4.372717 \times 10^{-8}t^3 + 1.64322 \times 10^{-10}t^4] \frac{\text{cal.}}{(\text{p.s.i.})(\text{mole } H_2O)}$$
$$- T_k \times 0.029683\,[-5.3255 \times 10^{-5} + 1.523064 \times 10^{-5}t - 1.311651 \times 10^{-7}t^2 + 6.57288 \times 10^{-10}t^3] \frac{\text{cal.}}{(\text{p.s.i.})(\text{mole } H_2O)}$$
$$+ [10^{935/T_k - 7.07894}][-5371.8 - 1.051p + 1.66 \times 10^{-3}(t - 25)^2 + 47.69t] \frac{\text{cal.}}{(\text{p.s.i.})(\text{mole } H_2O)} - p\,[10^{935/T_k - 7.07894}]\,(1.051) \frac{\text{cal.}}{(\text{p.s.i.})(\text{mole } H_2O)}$$

Phase Relations for H_2S–H_2O System. The lower thermodynamically stable temperature limit of safe operation is that at which formation of ice-like crystals of H_2S 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.

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

where 34.08 and 18.016 are the molecular weights of H_2S 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:

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

and

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

Variation of h over the range given would result in only 0.1% change in $(\text{P.E.})_G$, and variation of S would result in 1.0% change in $(\text{P.E.})_L$.
Similarly

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

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:

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

and

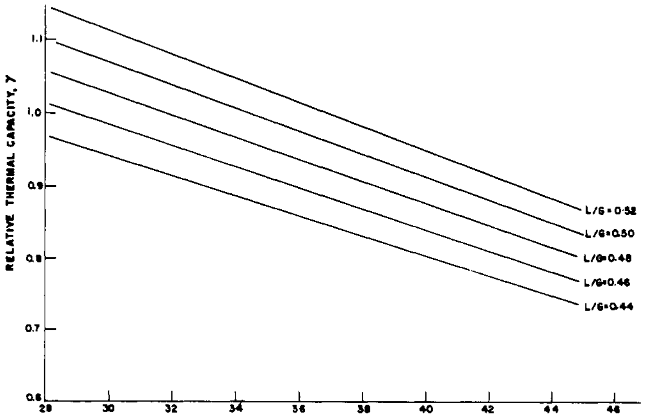

Figure 5. Variation of relative thermal capacity $\gamma = LC_L/GC_G$ with temperature and relative flow for countercurrent H_2S gas and H_2S at saturation equilibrium and at 250 p.s.i.a.

$$\frac{d(\text{P.E.})_L}{dz} = 0.0201, \text{ p.c.u./(pound-mole } H_2O\text{)(tray)}$$

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 Excahnge 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:

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

$$K_g = \frac{[D_2O]_g}{[D_2S]_g}\frac{[H_2S]_g}{[H_2O]_g} = 0.662e^{1466/RT_k}$$

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

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

$$K_g = 1.010e^{463/RT_k} = \frac{[HDO]_g\,[H_2S]_g}{[H_2O]_g\,[HDS]_g}$$

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

$$K_L = 0.871e^{593/RT_k} = \frac{[HDO]_l\,[H_2S]_g}{[H_2O]_l\,[HDS]_g}$$

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).
(2) Hull, H.L., Pohl, H.A., "Thermal Behavior of Countercurrent Equipment," E.I. du Pont de Nemours & Co., Wilmington, Del., U.S. Atomic Energy Comm., Research and Develop. Rept. **DP-97**, 1954, declassified March 15, 1957.
(3) Keenan, J.H., Kayes, F.G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
(4) Kelley, K.K., U.S. Bur. Mines Bull. **406**.
(5) Lange, N.A., "Handbook of Chemistry," 7th ed., Handbook Publ., Sandusky, Ohio.
(6) Selleck, F.T., Carmichael, L.T., Sage, B.H., *Ind. Eng. Chem.* **44**, 2219 (1952).
(7) Suess, A.E., FIAT Rev. Ger. Sci., Physical Chemistry (1939–1946), 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).

RECEIVED for review June 29, 1960. Accepted April 20, 1961. Work supported by Atomic Energy Commission at Explosives Dept., Atomic Division, E.I. du Pont de Nemours & Co., under Contract AT(07-2)-1. Article written with permission of Atomic Energy Commission and E.I. du Pont De Nemours & Co. at the Plastic Laboratory, Princeton University, Princeton, N. J., under Signal Corps Contract No. D-36-039sc-78105; DA Project 3-99-15-108; ONR 356-375; WADD Project 7371.

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)], 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.