Physical Properties of Hydrogen Sulfide-Water Mixtures

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Calculations concerning the production of heavy water by the hydrogen sulfide dual-temperature exchange process require precise data on the physical properties of dry hydrogen sulfide and hydrogen sulfide-water mixtures for temperatures between 25 and 170°C., and for pressures between 200 and 340 lb./sq.in.abs. However, data on enthalpy of hydrogen sulfide-water mixtures were not found in the literature, and data published on hydrogen sulfide-water compositions at equilibrium were given at such large intervals of temperature and pressure that they could not be interpolated accurately enough by ordinary means.

A study was undertaken to express the properties, listed below, with equations suitable for solution on a digital computer and useful in mathematical models of the process.

1. **Specific volume and enthalpy of dry, superheated hydrogen sulfide vapor,**
2. **Composition of hydrogen sulfide-water vapor and liquid in equilibrium,**
3. **Enthalpy of hydrogen sulfide vapor saturated with water vapor,**
4. **Enthalpy of water liquid saturated with hydrogen sulfide vapor,**
5. **Deuterium distribution constants for vapor-liquid equilibrium.**

New correlating constants were derived where needed. The equations and typical results are presented in this paper.

TABLE 1. CONSTANTS FOR EQUATIONS

	Equation			
	(1) to (4)	(5)	(6)	(7)
A	4.1497	9.6689	5.0375	0.066875
B	0.0514	9.1243	0.011280	1.4866×10^{-4}
C	0.02086	0.85231	2.0071×10^{-5}	6.1119×10^{-8}
D	0.02890	0.028290	1.5586×10^{-8}	3.4556×10^{-4}
E	1.79×10^{6}	0.056442	0.044033	4.5473×10^{-7}
F	—	6.8678×10^{-5}	5.7530×10^{-6}	2.6892×10^{-7}
G	—	1.8741×10^{-8}	8.0270×10^{-8}	3.3587×10^{-13}
H	—	0.023154		
J	—	7.6273×10^{-6}		
K	24.219	9.5097×10^{-10}		

	Equation			
	(8)	(9)	(11)	(15)
A	148.44	1112.6	2.5922	240.70
B	0.033299	5.0786	0.11344	20.688
C	2.4258×10^{-3}	0.020208	3.5701×10^{-4}	24.534
D	1.9610×10^{-6}	3.8312×10^{-5}	3.3231×10^{-7}	5.3049
E		2.5753×10^{-8}		0.52286

At the Savannah River Plant, a production facility operated by Du Pont for the U.S. Atomic Energy Commission, heavy water is produced by the hydrogen sulfide dual-temperature exchange process (*1*). To maintain production at minimal unit cost, process variables are controlled within limits determined by calculation of mathematical models of the process. To attain maximum benefits from this kind of control, relative values of the physical properties of hydrogen sulfide-water mixtures at equilibrium must be well defined.

Existing equations and techniques were used to calculate the thermodynamic properties of dry hydrogen sulfide and the deuterium distribution constants for vapor-liquid equilibrium; however, equations were derived to correlate published data on hydrogen sulfide-water composition, thermodynamic properties of water, heat of solution of hydrogen sulfide in water, and conditions for phase change in hydrogen sulfide-water mixtures. Constants for these equations are presented in Table 1.

DRY SUPERHEATED HYDROGEN SULFIDE

Specific Volume

The specific volume of hydrogen sulfide vapor was calculated by using the Beattie-Bridgeman equation (*2*) in the virial form.

TABLE 2. SPECIFIC VOLUME OF DRY H_2S VAPOR
(cu. ft./mole)

	Pressure, lb./sq.in.abs.				
°C.	250	280	300	320	380
30	20.09	17.51	16.05	14.77	—
50	22.14	19.42	17.90	16.56	15.38
70	24.07	21.20	19.60	18.19	16.95
90	25.92	22.89	21.21	19.73	18.43
110	27.71	24.52	22.75	21.20	19.83
130	29.46	26.11	24.25	22.62	21.19
150	31.18	27.67	25.72	24.01	22.51
170	32.88	29.20	27.16	25.38	23.80

$$P'V^4 - RTV^3 - \beta V^2 - \gamma V - \delta = 0 \qquad (1)$$

where: $\beta = RTB - A - RE/T^2$
$\gamma = -RTBD + CA - RBE/T^2$
$\delta = RBDE/T^2$

Equation (1) was solved for V by initially setting $V = RT/P$ and using the Newton-Raphson[*] method for successive approximations. In several trials, four repetitions produced a value of V which thereafter remained constant to the fifth significant place, but ten repetitions were programmed because computer time was less significant than sufficient precision.

The units were converted to cu.ft./lb. mole and cu.ft./lb. of gas for process calculations; results are shown in Table 2.[†]

Enthalpy

The enthalpy of hydrogen sulfide vapor was calculated by a method similar to that used by West (*3*) and Dodge (*4*). For superheated vapors,

$$H = H_o + \int_{T_o}^{T} C_p \, dT + \int_{T_o}^{P'} K \left[V - T \left(\frac{\delta V}{\delta T} \right)_P \right] dP' \qquad (2)$$

Substituting values from West:

$H_o = 4463 \pm 4$ cal./g. mole at 212.8°K., 1 atm.
$C_p = 7.15 + 0.00332\ T$

Thus:

$$\int_{T_o}^{T} Cp \, dT = \int_{T_o}^{T} (7.15 + 0.00332\ T) \, dT$$
$$= 7.15\,(T - T_o) + 0.00166\,(T^2 - T_o^2) \qquad (3)$$

The last integral of Equation (2) was evaluated by using the Beattie-Bridgeman equation with constants calculated by the method of Maron and Turnbull (*5*).

$$\int_{P_o}^{P'} \left[V - T \left(\frac{\delta V}{\delta T} \right)_P \right] dP'$$
$$= P'V - P_oV_o - \alpha \left(\frac{1}{V} - \frac{1}{V_o} \right)$$
$$- \sigma \left(\frac{1}{V^2} - \frac{1}{V_o^2} \right) + \eta \left(\frac{1}{V^3} - \frac{1}{V_o^3} \right) \qquad (4)$$

where: $\alpha = A + 3RE/T^2$
$\sigma = 3\ REB/2T^2 - CA/2$
$\eta = RBDE/T^2$

and other terms are the same as those in Equation (1).

The enthalpy at various temperatures and pressures was obtained by calculating V_o at 212.8°K. and 1 atm., and V at the applicable temperature and pressure with Equation (1). Each part of Equation (2) was then solved and the sum converted from cal./g. mole to pcu./mole and pcu./lb. of gas for process calculations; results are shown in Table 3.

TABLE 3. ENTHALPY OF DRY H_2S VAPOR
(p.c.u./mole)

	Pressure, lb./sq.in.abs.				
°C.	250	280	300	320	380
30	4,939	4,901	4,874	4,845	—
50	5,141	5,110	5,089	5,067	5,044
70	5,334	5,308	5,291	5,273	5,254
90	5,523	5,500	5,485	5,470	5,455
110	5,708	5,689	5,676	5,662	5,649
130	5,891	5,874	5,863	5,851	5,839
150	6,074	6,059	6,048	6,038	6,027
170	6,256	6,242	6,233	6,223	6,214

Comparison of Results

Specific volume and enthalpy of dry superheated hydrogen sulfide as calculated by computer and as displayed in West's tables differ by as much as 4%. The computer calculations are considered to be more precise because the computer carried eight significant digits.

HYDROGEN SULFIDE-WATER MIXTURES

The composition of gas and aqueous liquid phases at

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[*] Newton-Raphson method directs successive trials with the equation $V_{n+1} = V_n - f(V_n)/d[f(V_n)]$ where $f(V_n)$ is Equation (1) solved with V_n and $d[f(V_n)]$ is the first derivative of Equation (1) with respect to V_n.

[†] Tabular material has been deposited as document NAPS-00288 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $1.00 for microfiche or $3.00 for photocopies. Abridged versions are included in this paper.

equilibrium over wide ranges of temperature and pressure had been measured by Selleck (6). The data are presented in such large intervals that precise plots could not be adequately interpolated for the narrow ranges of temperature and pressure needed. More precise interpolations were made with correlating equations. However, no single equation was found which correlated either the humidity or the solubility data using all of the published information. It was necessary first to plot isotherms from all of Selleck's data, and from these to obtain points for isobars over the range of interest. Data from the isobars were correlated with the following equations.

Humidity

Temperature range: hydrate point to 171°C. [see Equation (13) for hydrate point].
Pressure range: 100 to 400 lb./sq.in.abs.

$$\ln Y = -A - B(\ln P) + C(\ln P)^2 - D(\ln P)^3 + E(T) - F(T)^2 + G(T)^3 + H(T)(\ln P) - J(T)^2(\ln P)^2 + K(T)^3(\ln P)^3 \tag{5}$$

Solubility: Low Temperatures

Temperature range: hydrate point to 100°C
Pressure range: 100 to 400 lb./sq.in.abs.

$$\ln X = A + BP - CP^2 + DP^3 - ET + FT^2 + GT^3 \tag{6}$$

Solubility: High Temperatures

Temperature range: 100 to 171°C.
Pressure range: 100 to 400 lb./sq.in.abs.

$$X = -A + BP - CP^2 + DT - ET^2 - FPT + GP^2T^2 \tag{7}$$

Typical results are shown in Tables 4 and 5. Most of the calculated values were within 1% of those obtained by Selleck. This small variation from experimental values resulted primarily from the initial cross plotting.

TABLE 4. COMPOSITION OF H_2S-H_2O VAPOR
(mole fraction of H_2O in H_2S)

Pressure, lb./sq.in.abs.

°C.	250	280	300	320	340
30	0.00349	0.00326	0.00314	0.00303	—
50	0.00915	0.00849	0.00812	0.00780	0.00752
70	0.02169	0.01994	0.01897	0.01813	0.01739
90	0.04682	0.04267	0.04040	0.03843	0.03670
110	0.09280	0.08395	0.07914	0.07500	0.07140
130	0.1703	0.1532	0.1440	0.1360	0.1292
150	0.2922	0.2618	0.2456	0.2318	0.2199
170	0.4724	0.4227	0.3964	0.3742	0.3553

TABLE 5. COMPOSITION OF H_2S-H_2O LIQUID
(mole fraction of H_2S in H_2O)

Pressure, lb./in.sq.abs.

°C.	250	280	300	320	340
30	0.02382	0.02680	0.02879	0.03077	—
50	0.01702	0.01915	0.02057	0.02199	0.02340
70	0.01300	0.01463	0.01571	0.01680	0.01788
90	0.01066	0.01200	0.01288	0.01377	0.01466
110	0.00944	0.01062	0.01139	0.01216	0.01292
130	0.00818	0.00929	0.01002	0.01074	0.01146
150	0.00658	0.00761	0.00830	0.00898	0.00967
170	0.00463	0.00559	0.00624	0.00689	0.00754

Enthalpy of Hydrogen Sulfide-Water Vapor

The enthalpy of the mixture was obtained by first calculating the enthalpy of each pure component at full system temperature and pressure. The mole fraction of each component was then calculated with Equation (5) and these mole fraction molar enthalpy products were summed to obtain the system enthalpy.

The molar enthalpy of hydrogen sulfide gas was calculated with Equation (2). The molar enthalpy of water vapor was calculated by adding the enthalpy of liquid water to the heat of vaporization at the problem temperature and at the water vapor-liquid saturation pressure. In this method, the effect of pressure on the heat of vaporization is assumed to be negligible. The equation of Keenan and Keyes (7) for enthalpy of superheated water vapor cannot be used directly because the pressure of water vapor saturating hydrogen sulfide gas is less than the water vapor-liquid saturation pressure. Keenan and Keyes' data for enthalpy of liquid water and heat of vaporization were correlated to within 0.1% of the published values with Equations (8) and (9).

Enthalpy, pcu./lb. of liquid water =

$$-A + BT + CT^2 - DT^3 \tag{8}$$

$$\Delta H = A - BT + CT^2 - DT^3 + ET^4 \tag{9}$$

The enthalpies were converted to pcu./mole and calculations made over the range of pressures of interest; results are shown in Table 6. No experimental data were found for comparison.

TABLE 6. ENTHALPY OF H_2S SATURATED WITH H_2O VAPOR
(p.c.u./mole of gas)

Pressure, lb./sq.in.abs.

°C.	250	280	300	320	340
30	4,961	4,921	4,893	4,865	—
50	5,196	5,162	5,138	5,114	5,090
70	5,464	5,428	5,405	5,382	5,360
90	5,800	5,755	5,727	5,700	5,675
110	6,253	6,184	6,143	6,107	6,073
130	6,882	6,768	6,704	6,648	6,598
150	7,752	7,566	7,465	7,377	7,300
170	8,926	8,637	8,483	8,351	8,237

Enthalpy of Hydrogen Sulfide-Water Liquid

The molar enthalpies of pure components were combined with the heat of solution to obtain the enthalpy of the liquid mixture (8).

$$H_s = XH_1 + (1 - X)\,H_2 - XQ \tag{10}$$

Equations for X, H_1, and H_2 have been given. The heat of solution data presented by Pohl and Hull (9) were correlated with the following equation.

$$\ln H_x = -A + BT - CT^2 + DT^3 \tag{11}$$

H_x was converted to pcu./mole to obtain Q in Equation (10).

The variation of system enthalpy with temperature and pressure is shown in Table 7. Again, no experimental data were found for comparison.

TABLE 7. ENTHALPY OF LIQUID H_2O SATURATED WITH H_2S (p.c.u./mole of liquid)

°C	Pressure, lb./sq.in.abs. 250	280	300	320	340
30	645.6	657.7	665.6	673.3	—
50	972.9	981.4	986.9	992.4	997.7
70	1,313	1,320	1,324	1,328	1,332
90	1,663	1,668	1,671	1,674	1,677
110	2,019	2,023	2,026	2,029	2,031
130	2,379	2,382	2,385	2,387	2,390
150	2,741	2,744	2,747	2,749	2,751
170	3,108	3,111	3,113	3,115	3,117

Overall Distribution Constant

The distribution constant β relating the concentration of deuterium in gas (y) and liquid (x) phases was calculated with equations given by Bebbington and Thayer (*1*) as follows:

$$\beta = \frac{x(1-y)}{y(1-x)} = \frac{(1+H')(S+K)}{\alpha(1+S)(1+H'K)} \qquad (12)$$

where: $\alpha = 1.1596\ e^{-65.43/T}$

$K = 1.010\ e^{-233/T}$

Typical results are shown in Table 8. A comparison of these results with previous results (*1*) shows that the improved interpolations of humidity and solubility data had minor effect (−2.3%) at high temperatures, and no effect at low temperatures, on the calculated β's.

TABLE 8. DEUTERIUM DISTRIBUTION CONSTANT (β) Pressure, lb./sq.in.abs.

°C.	250	280	300	320	340
30	2.2915	2.2884	2.2862	2.2840	—
50	2.1526	2.1517	2.1510	2.1501	2.1492
70	2.0213	2.0231	2.0239	2.0245	2.0248
90	1.8897	1.8954	1.8984	1.9009	1.9030
110	1.7507	1.7621	1.7682	1.7735	1.7780
130	1.6010	1.6198	1.6300	1.6388	1.6464
150	1.4415	1.4684	1.4831	1.4958	1.5067
170	1.2771	1.3112	1.3299	1.3460	1.3601

Phase Change

It would be misleading to report any values for hydrogen sulfide-water mixtures at conditions where hydrate forms or where hydrogen sulfide gas liquifies. Selleck's data on hydrogen sulfide-water phase behavior lead to the following equations for phase change.

$$\text{Hydrate temperature, °C.} = 9.3987 \ln P - 24.85 \qquad (13)$$

$$\text{Hydrogen sulfide boiling point, °C.} = 47.558 \ln P - 245.53 \qquad (14)$$

In each calculation, the problem temperature was compared with the hydrate and boiling point temperatures at the problem pressure. If the problem temperature was greater, the problem continued, otherwise a value of zero was reported by the program for the property being calculated.

Similarly, each calculation involving dry hydrogen sulfide was tested for hydrogen sulfide vapor-liquid saturation. West's data for hydrogen sulfide saturation conditions were correlated with the following equation.

$$T = A - B \ln P + C\ (\ln P)^2 - D\ (\ln P)^3 + E\ (\ln P)^4 \qquad (15)$$

CONCLUSION

This study was undertaken to provide information necessary for the improvement of techniques used in the production of heavy water. The paucity of published data on state functions and other parameters applicable to the hydrogen sulfide-water system indicates that this new information would be useful to others concerned with such a system. The repetitive nature of some of the calculations makes them particularly adaptable to computer techniques. It is primarily because of this that the nonempirical values given in this paper are better than those previously available. Further, the values for enthalpy of hydrogen sulfide-water mixtures are the only ones known to be available.

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NOTATION

P' = pressure, atm.
P = pressure, lb./sq.in. abs.
V = volume, liters/g.mole
T = temperature, °K.
R = gas constant, liter atm./g.mole — °K. = 0.08206
H = enthalpy at T and P' above H_o in cal./g. mole
H_o = enthalpy of hydrogen sulfide vapor at 1 atm. and 212.8°K.
T_o = temperature at the zero state, °K.
C_p = specific heat capacity at constant pressure, cal./(g. mole) (°K.)
P_o = pressure at zero state (1 atm.)
H_1 = enthalpy of dissolved hydrogen sulfide vapor, pcu/mole of hydrogen sulfide
H_2 = enthalpy of liquid water, pcu/mole of water
Q = heat of solution, pcu/mole of hydrogen sulfide dissolved
H' = humidity, moles water/mole of hydrogen sulfide gas
S = solubility, moles hydrogen sulfide/mole of water liquid
X = mole fraction hydrogen sulfide in water liquid
Y = mole fraction water in hydrogen sulfide gas
H_x = enthalpy, cal./g. mole hydrogen sulfide dissolved in water
ΔH = heat of vaporization, pcu/lb. of water
H_s = enthalpy of hydrogen sulfide-water solution, pcu/mole
p.c.u. = pound centigrade unit

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