Technical Data Book: Chapter 9 – Phase Equilibrium in Systems Containing Water

API TECHNICAL REPORT TDB-9
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SCOPE

Technical Report TDB-9 provides methods for estimating the vapor-liquid, vapor-liquid-liquid and vapor-liquid-hydrate equilibria of mixtures of water with pure components and petroleum fractions that are common in refinery applications. Computer algorithms and figures are presented calculating the phase extents and compositions of these mixtures. An estimate of the accuracy and range of application for each method is presented.

Any references to other chapters within this document refer to the corresponding Technical Data Book Chapter which is published as API Technical Report TDB-x, where x is the chapter number.

9-0 Introduction

Water Solubilities

Water-containing systems of interest to the petroleum and natural gas industries involve all three states: vapor, liquid and solid. These systems are characterized by partial miscibility in the liquid phase under certain conditions. Sources of phase equilibria data for water-hydrocarbon systems are listed in Table 9-0.2. Data marked as rejected in Table 9-0.2 were found to be inconsistent and were not used in the development of this chapter. Data marked as not evaluated were added to Table 9-0.2 after the completion of the chapter. Additional water-hydrocarbon solubility references can be found in the IUPAC Solubility Data Series (199a). A partial listing of sources of data for solubilities of nonhydrocarbon gases in water is given in Table 9-0.3.

Water-Hydrocarbon Mutual Solubilities

In all binary water-hydrocarbon systems, the complete phase relations are described by a three-dimensional pressure-temperature-composition diagram. As an example of the solubility relationships, pressure-composition slices at three different constant temperatures are shown in Figure 9-0.1. In each, the solubilities (liquid-phase composition) are given by the heavy lines. As indicated, these solubilities occur at low pressures in a vapor-liquid equilibrium system and at high pressures in a liquid-liquid equilibrium systemAt an intermediate pressure, vapor–liquid–liquid equilibrium (VLLE) can occur. For a water-hydrocarbon binary system with three coexisting phases, the Gibbs phase rule gives one degree of freedom; At a fixed temperature, the equilibrium pressure and phase compositions are uniquely determined. In binary water–hydrocarbon systems with negligible mutual solubility, this three-phase pressure can be approximated as the sum of the pure-component vapor pressures at the system temperature.

The three-phase solubilities for water in many hydrocarbons are given in Procedure 9A1.1 and for hydrocarbons in water in Procedure 9A2.1. The solubilities of some solid polynuclear aromatics in water are given in Procedure 9A2.3 and the solubilities of water in liquid hydrocarbon mixtures are given in Procedure 9A1.3. Procedure 9A1.5 is used to calculate the solubility of water in pure hydrocarbons and hydrocarbon mixtures whenever Procedures 9A1.1 and 9A1.3 cannot be used. The solubility of hydrocarbons in water under vapor-liquid-liquid equilibrium conditions at 77°F is given in Procedure 9A2.6.

As shown in Figure 9-0.1, pressure has an appreciable influence on solubility in the vapor-liquid region and a very small influence in the liquid-liquid region. Thus, although Procedure 9A1.1 and Procedure 9A2.1 are directly applicable only to vapor-liquid-liquid equilibrium, the procedures are good approximations of the solubility at pressures above the sum of the vapor pressures of the components where only two liquid phases exist. Procedure 9A2.3 is equivalent to Procedure 9A2.1; the only difference is that the hydrocarbon-rich phase is solid in this case. The influence of pressure on the solubilities is even smaller. The equilibrium phases are hydrocarbon-rich solid in equilibrium with water-rich liquid with or without a vapor phase.

Small amounts of impurities or minor components can seriously alter the solubility characteristics of a mixture. For example, if a small amount of an aromatic hydrocarbon is present as an impurity in a predominantly paraffin system, the mutual solubility with water will be increased more than would be predicted from a molar average solubility for the hydrocarbons. More predictable behavior is expected for mixtures of hydrocarbons from a single homologous series.

Solubilities of Hydrocarbon and Nonhydrocarbon Gases in Water

The water content of natural gases in contact with liquid water at 60°F and 14.7 psia is given in Procedure 9A3.1 together with a salinity correction factor. The salinity correction factor is to be used if salt is in the liquid-water phase. The solubility of hydrocarbons in aqueous salt solutions is given in Procedure 9A5.1. Procedure 9A6.1 is a computer method for phase equilibrium calculations in water-hydrocarbon systems using the modified Soave-Redlich-Kwong equation of state.

Henry's constants for selected gases in water are given in Procedure 9A7.1. This procedure is valid only for low and intermediate pressures (0 to 400 psig). Equilibrium concentrations of binary and ternary sour gas systems in water are given in Procedure 9A7.3 and the pH of ammonia and hydrogen sulfide in water is given in Procedure 9A8.1.

Salt Effects on Solubilities of Hydrocarbons and Nonhydrocarbon Gases in Water

Salt effects on the solubilities of nonelectrolytes in water are very complex and difficult to model. Most salts have a salting-out effect on nonpolar solutes (i.e., the solubility of the solute decreases as the salt concentration increases) but some salts have the reverse effect. For a polar solute, the effect of each salt is different. Solubilities in water as a function of salt concentration can generally be correlated by an empirical relationship known as the Setschenow equation (128a, 197a).

Table 9A5.2 gives literature sources and Setschenow constants for solubilities of hydrocarbons in different aqueous salt solutions. Table 9-0.4 gives a partial listing of literature sources for the salt effects on solubilities of nonhydrocarbon gases in water.

Gas Hydrates

In the most common water-light-hydrocarbon phase equilibria, which involve a solid phase, the solid phase is a gas hydrate. The hydrate has a network of hydrogen-bonded water molecules with small cavities distributed throughout the solid structure in a well-defined pattern. The structure is stabilized only when some or all cavities contain small "solute" molecules which interact weakly with the water through forces like those between molecules in a liquid. The gas hydrate is not a chemical compound: it is a clathrate inclusion compound.

Two different structures exist (Types I and II) each having two different size cavities. The smallest size solute molecules (top group of Table 9-0.5) fit into all the cavities in Structure I, slightly larger molecules (middle group of Table 9-0.5) fit into only the large cavities in Structure I, and larger molecules (bottom group of Table 9-0.5) fit into the large cavities of Structure II. Structure II hydrates will not form with all the cavities filled by a single solute. However, when a small molecule with strong hydrate-forming tendencies (such as hydrogen sulfide) is present, it can fit into the small and some of the large cavities to stabilize a Structure II hydrate containing large molecules (Table 9-0.6), which would not otherwise form a hydrate. Molecules larger than those in Table 9-0.6 will not form hydrates because the water molecules encaging the solute would be too distant to form the hydrogen bonds that stabilize the structure.

As indicated in Table 9-0.5, there exists for each group in the table a theoretical composition that corresponds to the definite ratio of filled cavities to water molecules in the structure. Experimentally determined compositions generally indicate the presence of slightly more water per mole of solute than predicted from the structure. This implies that more cavities than predicted are empty and that these clathrates are potentially nonstoichiometric compounds. The composition is relatively insensitive to pressure-temperature conditions, but a small effect has been reported.

Since hydrate compositions are fairly constant, the phase relations can be described by two dimensional pressure-temperature diagrams (see Figure 9-0.7), which are constant-composition slices from the complete three-dimensional cube. In these three diagrams, the hydrate region is in the low-temperature, high-pressure area to the left of the heavy lines. If the overall composition is that of the hydrate (F_2), hydrate alone will exist in this region, whereas if either excess water (e.g., overall composition F_1) or excess solute (e.g., F_3) is present, the excess will appear with the hydrate. The excess component will exhibit phase relations almost as if it were pure, so that a water melting-point line extends into the hydrate region for overall composition F_1, and the vapor pressure curve for the solute extends into the hydrate region for F_3. Similarly, outside the hydrate-forming region, the interactions between solute and water are so small that only very small melting-point depressions and boiling-point elevations are exhibited and the phase relations are essentially those of the pure components.

The upper quadruple point, where hydrate coexists with vapor solute, liquid solute and liquid water, is called the critical decomposition point. The implications of this title are misleading because hydrates can be made to coexist with liquid water and liquid solute above this critical decomposition temperature (T_{cd}) by using very high pressures.

The phase diagrams shown in Figure 9-0.7 are general for all systems except those containing compounds that have critical temperatures below room temperature. In this case, the solute cannot be liquefied to give an upper quadruple point, so no critical decomposition point occurs.

Hydrate systems typically exhibit strong metastable tendencies, so that it is difficult to initiate hydrate formation in the absence of the common nucleating influences such as excess pressure, supercooling, agitation and seeding. Similarly, the hydrate phase will occasionally persist in regions where decomposition is favored. Nucleation occurs most readily when the water phase is liquid but hydrates will also form in systems containing solid or vapor water.

The latter case can occur in natural gas transmission pipelines. As the water concentration of the system becomes progressively smaller (F_3, F_4, F_5, F_6), the dew-point pressure is increased (see last diagram in Figure 9-0.7) until the dew point line extends into the hydrate region. Below

this line in the hydrate region, the hydrate can be formed directly from vapor solute and vapor water.

Hydrate formation conditions for a number of binary systems containing water and hydrocarbons or related compounds are presented in Figures 9B1.1 and 9B1.2. Additional data for ternary systems containing two solutes are available in the literature (see Table 9-0.8). Figure 9B1.3 calculates the formation conditions for natural gases of various specific gravities relative to air. Since specific gravity does not satisfactorily characterize the composition of a natural gas, this procedure is accurate only to about 10 percent and errors of 40 percent in predicting formation pressures are possible.

Hydrate formation conditions may also be predicted accurately by the computer method given in Procedure 9B2.1. This procedure is complex and is recommended if many predictions will be made.

Hydrates are known primarily as nuisances that block natural gas pipelines. In a pipeline, hydrate formation conditions can be reached when the gas is cooled by expansion through a valve or some other constriction. Graphic correlations for determining the permissible expansions of natural gases of various specific gravities have been developed by Katz (67b) from Mollier diagrams and K charts. These charts (Figures 9B1.4 through 9B1.7) permit a very rapid determination of the amount of expansion ($\Delta H = 0$) that can occur in natural gases before hydrate formation conditions are reached.

Further information on gas hydrates is available in a number of reviews (9b, 10b, 14b, 16b, 20b, 26b-28b, 31b, 60b, 63b, 66b, 93b, 103b, 111b, 115b, 116b, 139b, 144b). The following are particularly comprehensive: Schroeder (111b), Deaton and Frost (31b), Parent (93b), Katz et al. (68b), Van der Waals and Platteeuw (144b), Kase (66b), and Byk and Fomina (16b).

Hydrate formation in gas pipelines may be avoided by addition of a suitable inhibitor such as methanol, ethylene glycol or diethylene glycol. Figures 9-0.9 and 9-0.10 are presented as typical examples of the higher pressures that may be used without danger of hydrate formation when inhibitors are present.

Knowledge of gas phase compositions on a water-free basis is needed to use of Procedure 9B2.1. However, recent research shows that water content of gases is an important factor in determining whether or not hydrates will form. Information and data for water content of methane and natural gases are found in References 1c and 35c.

More information on dehydration can be located in References 1c-36c. This list is not complete, and additional information sources on dehydration are given in References 31b, l0c, and 28c.

A comprehensive evaluation by T. E. Daubert of the GPA/SIM, Equiphase, GPA/AQUASIM, and API/HYDRATE programs with an extensive database was published by the Gas Processor's Association (150b) and is a recommended source to be consulted for both recent data and evaluations.

CSMHYD Program

Recent work and a prediction method CSMHYD on hydrates are given in a monograph by E. D. Sloan, Jr. (151b).

Figure 9-0.1 – Water-Hydrocarbon Solubility Phase Relations

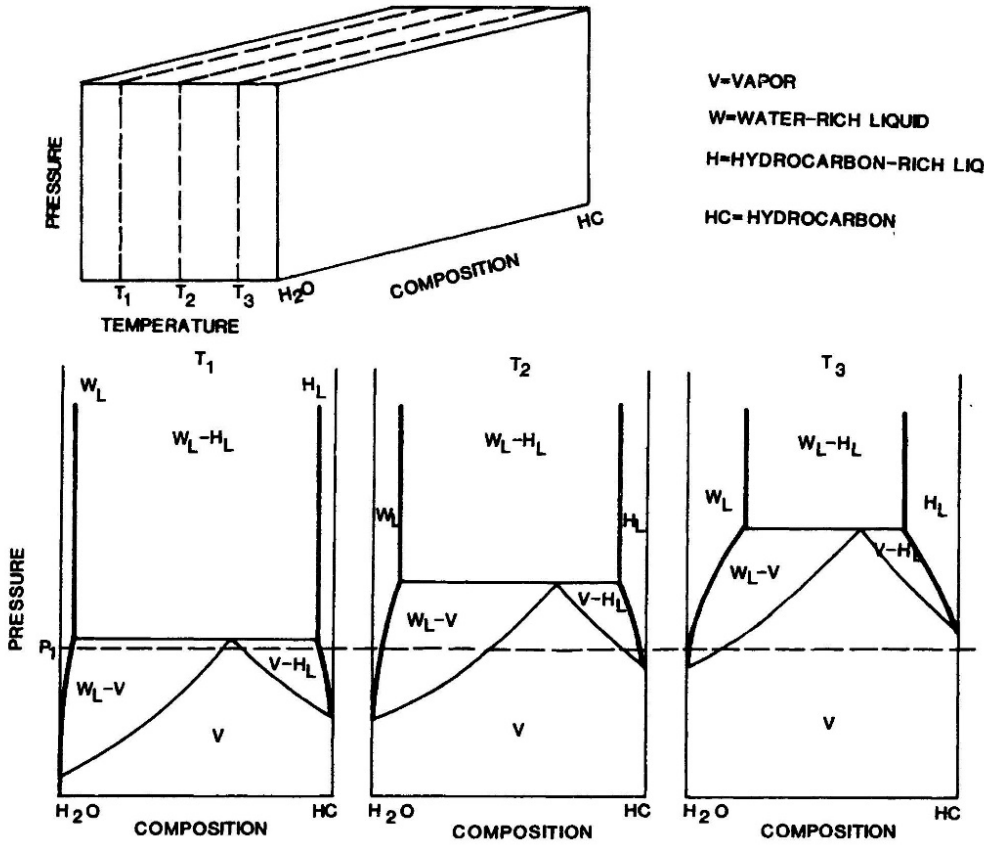


Table 9-0.2 – Literature Sources of Phase Equilibria Data for Water-Hydrocarbon Systems*

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
Paraffins						
methane	35-104	14.7	1	1	A	36a
	77	525-9680	1	1	A	41a
	77-340	200-10000	1	1	A	43a
	100-250	51-557	1	1	A	46a
	77-86	46-750	1	1	A	53a
	122-600	200-2450	1	1	A	67a
	65-100	14.7	1	1	A	120a
	77	14.7	1	1	A	136a
	77-302	590-5804	1	1	A	143a
	53-167	14.7	1	1	A	147a
	125-257	1470-8935	1	1	A	160a
	33-86	14.7	1	1	A	232a
	50-100	100-12000	1	1	R	47a
	77	550-1300	1	1	R	62a
	77	14.7	1	1	R	146a
	100-460	200-10000	3	1	R	158a
	302-662	100-28600	1	1	R	173a
	41-113	14.7	1	1	R	224a
ethane	35-104	14.7	1	1	A	36a
	77-212	330-528	3	1	A	38a
	100-340	200-1215	1	1	A	41a
	100-340	60-10000	1	1	A	42a
	662-672	2900-7250	4	1	A	44a
	392-752	2900-53664	6	3	A	44a
	77	14.7	1	4	A	136a
	54-162	14.7	1	1	A	147a
	90-100	441-735	2	2	A	149a
	100-460	200-10000	3	1	A	175a
	41-113	14.7	1	1	A	224a
	77	14.7	1	1	R	146a
	63-102	6-10	1	1	R	231a
propane	60-280	14.7-538	1	1	A	9a
	68-86	14.7	1	1	A	36a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	42-205.7	82-637	7	4	A	109a
	35-205.7		2	4	A	109a
	100-310	100-3000	4,6	1,3	A	109a
	77	14.7	1	4	A	136a
	54-165	14.7	1	1	A	147a
	60-187		5	4	A	168a
	39.2	14.7	1	1	A	221a
	41-113	14.7	1	1	A	224a
	63-102	5-8	1	1	A	231a
	60-130	10-100	1	1	R	48a
	39-122	14.7	1	1	R	113a
n-butane	100-220	1000-10000	6	3	A	26a
	68-86	14.7	1	1	A	36a
	671-687.2	3750-16000	6	3	A	44a
	100-280	20-1000	1	1,3,4	A	121a
	51-169	14.7	1	1	A	147a
	100-305.6	52-637.5	5	4,2	A	176a
	100-460	20-10000	4,6,7	1,3,4	A	177a
	37-66	14.7	1	1	A	182a
	41-113	14.7	1	1	A	224a
	41-69.8	40-94	2	3	R	18a
	50-104	29-82	1	3	R	104a
	39-122	14.7	1	1	R	113a
	77		1	4	R	136a
	39	14.7	1	1	R	221a
	100-280	52-490	7	4	R	223a
	63-102	4-6	1	1	R	231a
2-methylpropane	44-71		2	4	A	18a
(isobutane)	77		1	4	A	136a
	100-220	10-310	1	1	A	180a
	50-104	22-53	1	3	R	104a
	41-113	14.7	1	1	R	224a
n-pentane	41-77	14.7	2	3	A	18a
	572-665	2200-10000	1	1,3	A	39a
	64		1	4	A	63a
	100-400	120-2000	1	1	A	67a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	101–302	17–308	6	4	A	67a
	418–550	970–2700	2,6	4	A	78a
	77		1	4	A	115a
	77		1	4	A	136a
	68–159		1	4	A	150a
	39–86		1	4	A	154a
	41–95		1	4	A	166a
	32, 77		6	4	A	169a
	77–300		1	4	A	171a
	32–86		1	3	A	202a
	32–77		2	3	A	202a
	63–102	2–4	1	1	A	231a
	59–95		1	4	A	235a
	59–113		1	4	R	224a
	59–95		1	1	N	98a
2-methylbutane	42–71	14.7	2	3	A	18a
(isopentane)	32–68		2	4	A	56a
	77		1	4	A	121a
	68–140		1	6	A	163a
	77		1	4	A	171a
	32–77		2	3	A	202a
	32–77		1	3	A	202a
	77		1	4	R	136a
	32,77		6	4	R	169a
n-hexane	68		2	4	A	30a
	180–430	30–400	5	2	A	32a
	635.3–684.8		1	3	A	49a
	68–104		2	4	A	56a
	50–432		2	4	A	65a
	140		1	4	A	121a
	77		1	4	A	163a
	39.2–131		1	4	A	154a
	32–77		6	4	A	169a
	77–305		1	4	A	171a
	420–700	670–3220	4,5,6,7	1,2,3,4	A	178a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	77		2	4	A	183a
	32-77		2	3	A	202a
	32-131		1	3	A	202a
	77		2	4	A	206a
	392-428	711-11386	2	2	A	207a
	392-428	290-711	2	2	A	208a
	68		2	4	A	215a
	100-392	6-510	1	4	A	216a
	104-392	6.6-520	2	4	A	216a
	59-95		1	4	A	235a
	68	14.7	2	3	R	18a
	69-104		2	4	R	56a
	77		1	4	R	112a
	100-280	20-500	1	3	R	117a
	77		1	4	R	123a
	611-754	2408-19681	6	4	N	50a
	59-95		1	1	N	98a
	392-428	290-754	2	1	N	151a
2-methylpentane	77		1	4	A	136a
	77-301		1	4	A	171a
	32-77		6	3	A	202a
	572-600	2000-10000	1	1,3	R	39a
	77		1	4	R	123a
	32,77		6	4	R	169a
3-methylpentane	77		1	4	A	136a
	32-77		6	3	A	202a
	32,77		6	4	R	169a
	77		1	4	R	171a
2,2-dimethylbutane	77		1	4	A	136a
	77		1	4	A	171a
	32,77		6	4	R	169a
2,3-dimethylbutane	32-122		2	4	A	56a
	77-301		1	4	A	171a
	32-77		6	3	A	202a
	32,77		6	4	R	169a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
n-heptane	77-104		2	4	A	17a
	160.7-368.6		1	4	A	79a
	32- 77		6	4	A	169a
	77-303		1	4	A	171a
	59-368		1	4	A	199a
	77-113		1	3	A	202a
	32-77		2	3	A	202a
	59-95		1	4	A	235a
	50-77	14.7	2	3	R	18a
	560-670	2500-10000	1	1,3	R	39a
	32-122		2	4	R	56a
	63		1	4	R	63a
	72		1	4	R	66a
	387-550		5,6	4	R	78a
	77		1	4	R	112a
	77		1	4	R	136a
	77		2	4	R	192a
	59-65		1	1	N	98a
2-methylhexane	50-86		2	4	A	56a
	77		1	4	A	171a
3-methylhexane	32-77		6	3	A	202a
	32,77		6	4	R	169a
	77		1	4	R	171a
2,2-dimethylpentane	77		1	4	A	171a
2,3-dimethylpentane	77		1	4	A	171a
2,4-dimethylpentane	77		1	4	A	136a
	32-77		1,2	3	A	202a
	32-77		6	4	R	169a
	77		1	4	R	171a
3,3-dimethylpentane	77-303		1	4	A	171a
2,2,3-trimethylbutane	32-122		2	4	A	56a
n-octane	100-535	18-1285	7	4	A	22a, 88a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	32-77		6	4	A	169a
	77-300		1	4	A	171a
	32-77		1	3	A	202a
	32-77		2	3	A	202a
	437-509	508-11386	2	2	A	207a
	510.7	1075	7	4	A	88a
	300-531	97-1320	6,7	3,4	A	228a
	59-95		1	4	A	235a
	68	14.7	2	3	R	18a
	50-86		2	4	R	56a
	64		1	4	R	63a
	77		1	4	R	112a
	77		1	4	R	136a
	59-95		1	1	N	98a
3-methylheptane	77		1	4	R	171a
2,4-dimethylhexane	50-86		2		A	56a
2,2,4-trimethylpentane	50-68		2	4	A	56a
	434-490	265-915	2,5,7	5	A	78a
	77		1	4	A	136a
	40-75		2	4	A	153a
	32-77		6	3	A	202a
	32-77		6	4	R	169a
	77		1	4	R	171a
2,3,4-trimethylpentane	32-77		6	3	A	202a
n-nonane	77-278		1	4	A	171a
	77		2	4	A	192a
	59-68		1	4	A	235a
	77		1	4	R	112a
	59-68		1	1	N	98a
2-methyloctane	50-86		2	4	R	56a
3-methyloctane	50-86		2	4	R	56a
4-methyloctane	77		1	4	R	171a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
2,6-dimethylheptane	50-86		2	4	R	56a
2,2,5-trimethylhexane	77		1	4	A	136a
	32-77		6	3	A	202a
	32, 77		6	4	R	169a
n-decane	77, 104		2	4	A	192a
	302-590	75-11386	2	2	A	151a
	437-554	421-11386	2	2	A	208a
	77		1	4	R	11a
	77		1	4	R	60a
	346-624	120-2145	5,7	4	R	78a
	77		1	4	R	112a
2,7-dimethyloctane	50-86		2	4	R	56a
n-undecane	77		1	4	R	112a
	77-104		2	4	R	192a
n-dodecane	77		1	4	R	60a
	77-104		2	4	R	192a
	77		1	4	R	209a
n-tridecane	77-104		2	4	R	192a
n-tetradecane	77		1	4	R	60a
	104		2	4	R	192a
	77		1	4	R	209a
n-hexadecane	482-617	566-11386	2	2	A	207a
	68-122		2	4	R	56a
	77		1	4	R	60a
	77-104		2	4	R	192a
	77		1	4	R	209a
7,8-dimethyltetradecane	68-122		2	4	R	56a
n-octadecane	77		1	4	R	11a
	77		1	4	R	209a
n-eicosane	77		1	4	A	209a
n-hexacosane	77		1	4	A	209a
n-hexatriacontane	77		1	4	A	11a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
Naphthenes						
cyclopropane	70-220	14.7-500	1	1	A	93a
cyclopentane	77		1	4	A	136a
	77-308		1	4	A	171a
	77		1	3	A	202a
	32-104		2	4	R	56a
	127-389		1	4	R	81a
methylcyclopentane	243-389		1	4	A	81a
	77		1	4	A	136a
	77		1	3	A	202a
	50-86		2	4	R	56a
	77		1	4	R	81a
ethylcyclopentane	159-397		1	4	A	81a
	50-86		2	4	R	56a
n-propylcyclopentane	77		1	4	A	171a
isopropylcyclopentane	50-86		2	4	R	56a
1,1,3-trimethylcyclopentane	77		1	4	A	171a
n-butylcyclopentane	50-86		2	4	R	56a
n-pentylcyclopentane	77		1	4	R	171a
n-hexylcyclopentane	50-86		2	4	R	56a
2-cyclopentyloctane	50-86		2	4	R	56a
1,4- dicyclopentylbutane	50-86		2	4	R	56a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
cyclohexane	68-112		2	4	A	15a
	36.6-299.3	3786-25266	1	3	A	24a
	68		1	4	A	30a
	202-460	25-400	5	2	A	32a
	59-86		2	4	A	70a
	50-104		2	4	A	72a
	77-429		1	4	A	79a
	77-324		1	4	A	81a
	77		2	4	A	96a
	68		1	4	A	110a
	77		1	4	A	111a
	77		2	4	A	115a
	100-280	14.7-450	1	3	A	116a
	77		1	4	A	129a
	77		1	4	A	136a
	41-113		1	4	A	166a
	347-482	95-3400	2,4,5,6,7	4	A	178a
	77		2	4	A	183a
	68-482		2	4	A	199a
	392-482	406-11386	2	2	A	199a
	41-133		1	4	A	199a
	61-77		1	3	A	202a
	57-128		2	4	A	212a
	392-482	406-11386	2	2	A	207a
	392-482.0		2	4	A	207a
	104-408	4.6-500	1	4	A	216a
	104-392	4.6-430	2	4	A	216a
	77		2	4	A	235a
	68	14.7	2	3	R	18a
	50-122		2	4	R	56a
	378-536 378-556	325-2150	2,3,4,5,6	4	R	78a
	77		1	4	R	105a
	57-128		2	4	R	153a
	77		1	4	R	171a
	74.5		1	4	R	195a
	68		2	4	R	213a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
methylcyclohexane	154-419		1	4	A	81a
	77		1	4	A	115a
	77		1	4	A	136a
	77-301		1	4	A	171a
	77		1	4	A	199a
	77		1	3	A	202a
	50-86		2	4	R	56a
	349-547	195-1450	6,7	4	R	78a
	0-110		2	4	R	153a
ethylcyclohexane	100-535	17-1280	7	4	A	22a, 88a
	174-415		1	4	A	81a
	300-500	100-1495	1,3,7	3	A	228a
1-*cis*-2-dimethylcyclohexane	77		1	4	A	136a
1,4-dimethylcyclohexane	135-464		1	4	R	81a
	77		1	4	R	171a
1,1,3-trimethylcyclohexane	77		1	4	R	171a
n-butylcyclohexane	100-530	30-1031	7	4	A	22a
cycloheptane	77		1	4	R	136a
cyclooctane	77		1	4	R	136a
Olefins						
ethene (ethylene)	95-216	122-7701	1	1	A	20a
	100-250	14.7-500	1	1	A	45a
	302-572	1450-10000	1	1	A	186a
	59-77	350-1650	3	1	R	52a
	77	14.7	1	1	R	136a
	56-163	14.7	1	1	R	147a
propene (propylene)	70-220	14.7-500	1	1	A	10a
	100-280	50-5000	4	1	A	125a
	100-160	500-4500	6	3	A	125a
	100-198		7	4	A	125a
	334-662	1450-43512	4	1	A	186a
	70-106		2	4	R	64a
	50-104	100-235	1	3	R	104a
	77		1	4	R	136a
	77	8.5	1	1	R	137a
	77	10-14	1	1	R	138a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
2-methylpropene	42-70	59-74	2	3	R	18a
(isobutene)	50-104	26-68	1	3	R	104a
	77		1	4	R	136a
	70-183		2	4	R	165a
1-butene	100-291.2	10-1000	3	1,4,3	A	28a
	100-310	500-10000	6	3	A	124a
	77		1	4	A	136a
	42-71	42-49	2	3	R	18a
	100-291.2	10-624	3	1,4	R	27a
	100-280	60-560	7	4	R	223a
2-butene	77		2	3	R	18a
1-pentene	77		1	4	A	136a
2-pentene	77		1	4	A	136a
2-methyl-2-butene	59-77		1	4	A	152a
	68-140		2	3	A	163a
	104-140		1	4	A	163a
	50		2	4	R	56a
	421-515	970-2810	6	4	R	78a
3-methyl-1-butene	77		1	4	R	136a
1-hexene	100-430	30-780	7	4	A	22a
	77		1	4	A	136a
	77		1	4	A	152a
	77		1	4	A	199a
	77		1	3	A	202a
	198-405		2	4	R	32a
	86		2	4	R	56a
	540	2030	6	4	R	78a
	77		1	4	R	123a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
2-methyl-1-pentene	77		1	4	A	136a
4-methyl-1-pentene	77		1	4	A	136a
2,3-dimethyl-1-butene	86		2	4	R	56a
1- heptene	68-86		1	4	A	152a
	50-70	14.7	2	3	R	18a
	50-86		2	4	R	56a
2-heptene	77		1	4	A	136a
	77		1	4	R	152a
	74.5		1	4	R	195a
1-octene	100-530	95-1343	6	4	A	22a
	77		1	4	R	136a
	77		1	4	R	152a
1-octene, 2-octene mixture	50-86		2	4	R	56a
1-decene	59-77		1	4	A	152a
Diolefins						
1,3-butadiene	57-69		2	4	A	18a
	–40-140		2	4	A	73a
	–4-98.6		2	4	A	144a
	100-220	10-275	1	1	A	181a
	77		1	4	R	136a
	77	8.5	1	1	R	137a
1,4-pentadiene	77		1	4	R	136a
2-methyl-1,3-butadiene	68-140		6	4	A	163a
	77		1	4	R	136a
1,5-hexadiene	56-69	14.7	2	3	R	18a
	77		1	4	R	136a
1,6-heptadiene	77		1	4	R	136a
cyclopentene	77		1	4	R	136a
	77		1	4	R	152a
cylcohexene	50-104		2	4	R	56a
	77		1	4	R	58a
	77		1	4	R	136a
	86		1	4	R	152a
	74.5		1	4	R	195a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
cycloheptene	77		1	4	R	136a
1-methylcyclohexene	77		1	4	R	136a
1,4-cyclohexadiene	77		1	4	A	136a
4-vinylcyclohexene	77		1	4	R	136a
Acetylenes						
ethyne (acetylene)	60-80	70-550	1	1	A	91a
propyne	70-220	5-200	1	1	A	94a
(methylacetylene)	77		1	4	R	136a
	32-140	5-14.7	1	1	R	200a
1-butyne	77		1	4	R	136a
	32-140	4-10	1	1	R	200a
3-buten-1-yne	32-140	5-11	1	1	R	200a
1-pentyne	77		1	4	R	136a
1-hexyne	77		1	4		136a
1-heptyne	77		1	4	R	136a
1-octyne	77		1	4	R	136a
1-nonyne	77		1	4	R	136a
1,6-heptadiyne	77		1	4	R	136a
1,8-nonadiyne	77		1	4	R	136a
Aromatics						
benzene	213-399	42-467	6	4	A	3a
	77		1	4	A	4a
	156.65		2	3	A	12a
	50		2	4	A	18a
	41-108		1	4	A	19a
	77-131	14.5-9065	1	3	A	21a
	40-67		1	4	A	29a
	68		2	3	A	30a
	187-440	25-400	5	2	A	32a
	70		2	4	A	37a
	500-572	1470-9733	1	1,3,4	A	39a
	32		2	4	A	56a
	41-102		1	4	A	61a
	50-104		2	4	A	72a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	37-171		2	4	A	76a
	50-490		1	4	A	80a
	41-157		2	4	A	90a
	77		2	4	A	96a
	59-95		2	4	A	102a
	77		1	3	A	105a
	100-280	14.7-825	1	3	A	118a
	77		1	4	A	136a
	49-121		2	4	A	148a
	550-560	3600	6	2,3	A	157a
	437-662	300-2800	4,5,6,7	1,2,3,4	A	179a
	77		2	4	A	183a
	50-86		2	4	A	185a
	437-560	682-111386	2	2	A	199a
	68-164		2	3	A	202a
	33-156		1	3	A	202a
	437-500	682-11386	2	2	A	207a
	100-460	1014-5014	6	3	A	214a
	104-212	4.4-438	6	4	A	216a
	104-515	4.4-1366	6	4	A	219a
	34-150		1	4	R	2a
	33-113		1	4	R	7a
	50-122		2	4	R	15a
	70		1	4	R	34a
	86		1	4	R	77a
	362-573	275-2745	1,2,5,6,7	4	R	78a
	212-572		1	4	R	95a
	50-79		2	4	R	99a
	77		1	4	R	108a
	77		1	4	R	123a
	77		1	4	R	129a
	77		1	4	R	135a
	77		1	4	R	147a
	68		6	4	R	155a
	32,77		6	4	R	169a
	77		1	4	R	171a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	392-675	300-2800	4,5,6,7	1,2,3,4	R	179a
	392-716	14.7-50000	4,6	1,3	R	193a
	74.5		1	4	R	195a
	76-160		2	4	R	203a
	41-164		2	4	R	212a
	50-122		1	4	N	14a
	77-122		6	4	N	74a
	77-95		2	4	N	97a
	49-149	0.17-3.62	2	4	N	161a
	41-113		1	4	N	188a
	73-164		2	4	N	204a
	68-175		1	4	N	218a
	50-72		6	4	N	220a
methylbenzene	211-393	22.2-343	6	4	A	3a
(toluene)	140		1	4	A	4a
	32-114		1	4	A	19a
	40-67		1	4	A	29a
	70		1	4	A	34a
	77		2	3	A	35a
	536-590	2131-6689	1	3	A	39a
	59-86		2	4	A	70a
	194-435		1	4	A	80a
	61-140		1	1	A	92a
	302-572		1	4	A	95a
	77		2	4	A	96a
	77		1	3	A	105a
	77		1	4	A	136a
	40-110		2	4	A	153a
	50-122		2	4	A	185a
	49-77	14.7	1	1	A	189a
	71.6		2	3	A	199a
	68		2	3	A	199a
	32-86		2	3	A	202a
	118-183		2	4	A	212a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	95-131	0 - 45000	1	3	R	21a
	32-122		2	4	R	56a
	60.8		2	4	R	63a
	86		1	4	R	77a
	77		1	4	R	108a
	77		1	4	R	129a
	77		1	4	R	147a
	32,77		6	4	R	169a
	77		1	4	R	171a
	74.5		1	4	R	195a
	77		1	4	R	210a
	68		2	4	R	213a
	51-121		1	4	R	224a
	77-95		2	4	N	97a
	59-113		1	4	N	188a
ethylbenzene	77		1	4	A	5a
	33-109		1	4	A	19a
	101-535	16.1-1246	6	4	A	22a
	40-67		1	4	A	29a
	239-452		1	4	A	82a
	77		1	4	A	108a
	77		1	4	A	136a
	11-149		2	4	A	145a
	95-149		1	4	A	145a
	59-113	14.7	1	1	A	189a
	68-77		1	4	A	199a
	64-122		2	3	A	202a
	32-77		1	3	A	202a
	86-212	20-33	1	3	A	247a
	77		1	4	A	210a
	563	1549	7	4	A	88a
	300-531	87-1200	6	3	A	228a
	50-86		2	4	R	56a
	77		1	4	R	63a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
	77		1	4	R	147a
	32,77		6	4	R	169a
	77		1	4	R	171a
	65-121		2	4	N	59a
	77-95		2	4	N	97a
	59-113		1	4	N	188a
dimethylbenzenes	302-482		1	4	R	95a
	0-110		2	4	R	153a
	68		2	4	R	213a
1,2-dimethylbenzene	77		1	4	A	4a
(*o*-xylene)	50-86		2	4	A	56a
	282-484		1	4	A	80a
	77		1	4	A	136a
	0-110		2	4	A	153a
	59-113	14.7	1	1	A	189a
	32-77		2	3	A	202a
	32-77		1	3	A	202a
	77		1	4	A	210a
	77		1	4	R	25a
	32,77		6	4	R	169a
	77		1	4	R	171a
	59-113		1	4	N	188a
1,3-dimethylbenzene	257-392	40.8-291	6	4	A	3a
(*m*-xylene)	77		1	4	A	4a
	33-103		1	4	A	19a
	261-462		1	4	A	80a
	153-519		1	4	A	174a
	59-113	14.7	1	1	A	189a
	32-158		6	3	A	202a
	77		1	4	A	210a
	50-86		2	4	R	56a
	312-604	80-2215	5,6,7	4	R	78a
	32,77		6	4	R	169a
	77		1	4	R	171a
	68-158		6	4	N	33a
	59-113		1	4	N	188a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
1,4-dimethylbenzene	77		1	4	A	4a
(*p*-xylene)	58-109		1	4	A	19a
	286-496		1	4	A	80a
	77		2	3	A	107a
	109-541		1	4	A	174a
	59-113	14.7	1	1	A	189a
	32-77		6	3	A	202a
	77		1	4	A	210a
	86-212	14.7-30	1	3	A	247a
	32,77		6	4	R	169a
	77		1	4	R	171a
	59-113	110-2615	1 6,7	4 4	N R	188a 78a
n-propylbenzene	186-432		1	4	A	82a
	77-113	14.7	1	1	A	189a
	59		1	3	A	202a
	77		1	4	R	5a
	59		1	4	R	63a
	77		1	4	R	108a
	59-113		1	4	N	188a
isopropylbenzene	77		1	4	A	5a
(cumene)	32-122		2	4	A	56a
	77-177		1	4	A	71a
	59-113	14.7	1	1	A	189a
	77		1	4	A	210a
	77		1	4	R	136a
	77		1	4	R	171a
	59-113		1	4	N	188a
1,2,4-trimethylbenzene	77		1	4	A	136a
	59-113	14.7	1	1	A	189a
	355-606	145-1915	6,7	4	R	78a
	77		1	4	R	171a
	77		1	4	R	210a
	59-113		1	4	N	188a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
1,3,5-trimethylbenzene	68-104		2	4	A	56a
(mesitylene)	59-113		1	4	A	187a
	77-113		1	1	A	189a
	86-212	20-35	1	3	A	247a
	77		1	4	R	5a
	244-412		1	4	R	80a
	527-752	14.7-36750	4,6	1,3	R	193a
	77		1	4	R	210a
	59-113		1	4	N	188a
1,2,3-trimethylbenzene	59-113	14.7	1	1	A	189a
	77		1	4	R	210a
	59-113		1	4	N	188a
n-butylbenzene	68-86		2	4	A	56a
	77		1	4	A	133a
	77-95		2	3	A	202a
	77		1	3	A	202a
	86-212	20-35	1	3	A	25d
	77		1	4	R	5a
	77		1	4	R	108a
	77		1	4	R	210a
	77-95		2	4	N	97a
sec-butylbenzene	50-86		2	4	A	56a
	77		1	4	A	171a
	77		1	4	R	5a
	77		1	4	R	210a
tert-butylbenzene	50-86		2	4	A	56a
	77		1	4	R	5a
	77		1	4	R	210a
1-methyl-4-isopropylbenzene	77		1	4	A	199a
(*p*-cymene)	50-86		2	4	R	56a
1,3-diethylbenzene	100-530	73.7-1026	6	4	A	22a
	355-649	110-2615	6,7	4	R	78a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
diethylbenzene (mixture)	32-122		2	4	R	56a
1,2,4,5-tetramethylbenzene	77		1	4	A	171a
1,3,5-trimethyl-2-ethylbenzene	68-104		2	4	R	56a
1,3,5-trimethyl-2-allylbenzene	68-104		2	4	R	56a
1,3,5-trimethyl-2-propylbenzene	68-104		2	4	R	56a
2-phenyl-2,4,6-trimethylheptane	50-86		2	4	R	56a
n-hexylbenzene	77		1	4	A	112a
	41-84.2		1	3	A	202a
p-diisopropylbenzene	100-530		6	4	A	22a
ethenylbenzene	44.6-149.0		1	4	A	119a
(styrene)	42.8-113		2	4	A	119a
	77		1	4	R	5a
naphthalene	77		1	4	A	4a
	32-109		1	4	A	19a
	77		1	4	A	55a
	77		1	4	A	108a
	77		1	4	A	130a
	77		1	4	A	135a
	46-90		1	4	A	194a
	32-167		1	4	A	222a
1-methylnaphthalene	77		1	4	A	55a
	32-122		2	4	A	56a
	77		1	4	A	130a
	46-90		1	4	A	194a
2-methylnaphthalene	77		1	4	A	55a
	77		1	4	A	130a
1,3-dimethylnaphthalene	77		1	4	A	130a
1,4-dimethylnaphthalene	77		1	4	A	130a
1,5-dimethylnaphthalene	77		1	4	A	55a
	77		1	4	A	130a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
2,3-dimethylnaphthalene	77		1	4	A	55a
	77		1	4	A	130a
2,6-dimethylnaphthalene	77		1	4	A	55a
	77		1	4	A	130a
1-ethylnaphthalene	77		1	4	A	130a
	4-90		1	4	A	194a
2-ethylnaphthalene	77		1	4	A	55a
1,4,5-trimethylnaphthalene	77		1	4	A	130a
tetrahydronaphthalene (tetralin)	302-482		1	4	A	95a
biphenyl	77		1	4	A	4a
	32.7-109		1	4	A	19a
	77		1	4	A	55a
	77		1	4	A	130a
	32-148		1	4	A	222a
	50-122		1	4	N	14a
fluorene	77		1	4	A	130a
	77		1	4	A	135a
	32-167		1	4	A	222a
diphenylmethane	77		1	4	A	4a
phenanthrene	77		1	4	A	4a
	77		1	4	A	55a
	77		1	4	A	108a
	77		1	4	A	130a
	48-86		1	4	A	134a
	77-84		1	4	A	135a
	46-90		1	4	A	194a
	32-167		1	4	A	222a
1-methylphenanthrene	43-86		1	4	A	134a
	77		1	4	A	135a
trans-stilbene	77		1	4	A	5a
bibenzyl	77		1	4	A	5a
1,1-diphenylethylene	77		1	4	A	5a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
anthracene	77		1	4	A	108a
	77		1	4	A	130a
	41-84		1	4	A	134a
	77-84		1	4	A	135a
	46-90		1	4	A	194a
	32-167		1	4	A	222a
2-methylanthracene	77		1	4	A	130a
	43-88		1	4	A	134a
	77		1	4	A	135a
9-methylanthracene	77		1	4	A	130a
9,10-dimethylanthracene	77		1	4	A	130a
triphenylene	77		1	4	A	108a
	77		1	4	A	130a
pyrene	77		1	4	A	108a
	77		1	4	A	130a
	77-84		1	4	A	135a
	54-90		1	4	A	194a
	32-167		1	4	A	222a
benz(*e*)pyrene	46-90		1	4	A	194a
fluoranthene	77		1	4	A	108a
	77		1	4	A	130a
	77-84		1	4	A	135a
1,2-benzofluorene	77		1	4	A	130a
2,3-benzofluorene	77		1	4	A	130a
chrysene	77		1	4	A	108a
	77		1	4	A	130a
	77, 84		1	4	A	135a
naphthacene	77		1	4	A	108a
	77		1	4	A	130a
1,2-benzathracene	77		1	4	A	108a
	77		1	4	A	130a
	77-84		1	4	A	135a
7,12-dimethyl-1,2-benzanthracene	77		1	4	A	130a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
1,2,5,6-dibenzanthracene	77		1	4	A	108a
acenaphthene	77		1	4	A	55a
	77		1	4	A	130a
	32-167		1	4	A	222a
perylene	77		1	4	A	130a
3,4-benzopyrene	77		1	4	A	130a
3-methylcholanthrene	77		1	4	A	130a
benzo (*g,h,i*) perylene	77		1	4	A	130a
coronene	77		1	4	A	130a
Miscellaneous Hydrocarbons						
indan	77		1	4	A	130a
	77		1	4	A	171a
decahydronaphthalene	68-104		2	4		56a
(decalin)	575	1515	6	4		78a
cycloheptatriene	86-122		2	4	A	56a
	77		1	4	A	136a
1-methyl-2-phenylcyclopentane	50-86		2	4	A	56a
2-ethyl-2-phenylcyclopentane	50-86		2	4	A	56a
1-phenyl-2-methyl-1-cyclopentene	86		2	4	A	56a
1-phenyl-5-methyl-1-cyclopentene	86		2	4	A	56a
bicyclodecane	77		1	4	A	171a
d-limonene			1	4	A	133a
Water and Petroleum Fractions						
kerosene	30-140		2	4	A	40a
	230-500	36-780	2	3	A	75a
	28-194		2	4	A	76a
naphtha	318-432	83-400	2	3	A	75a
lubricating oil	250-540	34-1000	2	3	A	75a
jp-3 fuel	0-140		2	4	A	114a
jp-4 fuel	–10-140		2	4	A	40a
gasoline	104-285		2	4	A	1a
	69-131		2	4	A	37a
	–10-80		2	4	A	40a
	44-104		2	4	A	51a

Table 9-0.2 (Continued)

System	Temperature Range (°F)	Pressure Range, psia	Type of Data[a]	Region of Equilibrium[b]	Data Status[c]	Reference
Wyoming Farmers whole crude	77-325		1	4	A	171a,172a
Flower Comm. Whole crude	77-360		1	4	A	171a,172a
Louisiana State whole oil	77-356		1	4	A	171a,172a
Amoseas Lake topped oil	77-336		1	4	A	171a,172a
Reedy Creek topped oil	77-356		1	4	A	171a,172a
Alaska topped oil	77-355		1	4	A	171a,172a
Union Moonie topped oil	77-360		1	4	A	171a,172a
No. 2 distillation fraction Ghawar crude oil (270-380 F fraction)	77-356		1	4	A	171a,172a
No. 3 distillation fraction Ghawar crude oil (380-459 F fraction)	77-363		1	4	A	171a,172a
No. 4 distillation fraction Ghawar crude oil (450-601 F fraction)	77-356		1	4	A	171a,172a
No. 5 distillation fraction Ghawar crude oil (601-700 F fraction)	77-360		1	4	A	171a,172a
Water and Defined Hydrocarbon Mixtures						
methane/n-butane	100-280	200-1912	7	4	A	140a
n-butane/1-butene	100-280	50-560	7	4	A	223a
methylbenzene-naphtha	525-576	1600-3000	6	3	A	8a
ethylene/ethane	100-280	200-5000	4	1	A	6a
benzene/n-hexane	77		1	4	A	123a
benzene/2- methylpentane	77		1	4	A	123a
benzene/1-hexene	77		1	4	A	123a
cyclohexane/n-hexane						
cyclohexane/2-methylpentane	77		1	4	A	123a
cyclohexane/1-hexene	77		1	4	A	123a

Type of Data

[a]1 = Solubility of hydrocarbon in the water-rich liquid
2 = Solubility of water in the hydrocarbon-rich liquid
3 = Composition of the vapor phase
4 = 1 and 3 at the same conditions
5 = 2 and 3 at the same conditions
6 = 1 and 2 at the same conditions
7 = 1, 2 and 3 at the same conditions

Region of Equilibrium

[b]1 = Water-rich liquid-vapor equilibrium region
2 = Hydrocarbon-rich liquid-vapor equilibrium region
3 = Water-rich liquid-hydrocarbon-rich liquid equilibrium region
4 = Water-rich liquid-hydrocarbon-rich liquid-vapor equilibrium region (except for some heavy aromatics for which the equilibrium is between water-rich liquid, solid hydrocarbon and vapor). No entry is made in the pressure range column for most of the data in this equilibrium region. In those cases, the study was performed at the vapor pressure of the system or at atmospheric pressure (in case of some heavy hydrocarbons) in an open-to-air system.

Data Status

[c]A = Accepted tested data
R = Rejected tested data (not used in chapter development)
N = Data not evaluated

Table 9-0.3 – Literature Sources of Data for Solubility of Nonhydrocarbon Gases in Water

Gas	Temperature Range (°F)	Pressure Range (psia)	Reference
methyl mercaptan	100-600	44-2067	24d
ethyl mercaptan	438-600	244-1929	24d
carbon disulfide	400	291.75	24d
carbonyl sulfide	400	291.75	24d
oxygen	37-95	14.7[a]	1d
	32-146	2-17	7d
	43-73	14.7	9d
	59-77	14.7	20d
	77	3-17	36d
	68	14.7	37d
	45-86	12-16	42d
	77	14.7	43d
	212-325	195-1410	55d
	43-75	14.7	63d
	212-550	14.7	64d
	68-158	14.7	83d
hydrogen	32-212	8.9-15	7d
	41-77	14.7	8d
	39-75	14.7	9d
	59-77	14.7	20d
	68	14.7	37d
	70-77	25-58	40d
	77	14.7	41d
	212-325	205-1455	64d
	32-122	13-17	82d
	32-140	14.7	85d
	100-600	37.8-1990[a]	22d
hydrogen sulfide	77	14.7	33d
	32	14.7	56d
	32-140	14.7	85d
	41-140	5-72	86d

Table 9-0.3 (Continued)

Gas	Temperature Range (°F)	Pressure Range (psia)	Reference
	100-340	100-3000	60d
	320-626	94-3100	34d
	100-600	48.9-1139[a]	22d
	300-600	96.8-2646[a]	23d
nitrogen	38-95	14.7	1d
	32-212	2.9-13	7d
	41-77	14.7	8d
	39-75	14.7	9d
	99.5	14.7	27d
	100.4	13.8-89	28d
	64-82	25-68	40d
	77	14.7	43d
	124.7	1470-81820	51d
	1124-257	1480-8940	52d
	68	14.7	65d
	66-176	14.7	83d
	32-336	1470-4410	27d
	77-212	367-14700	75d
	100-600	38.2-1995[a]	22d
ammonia	32	0.3-38	57d
	-182-356	0.3-290	11d
	176-248	6.9-29	79d
carbon monoxide	42-72	14.7	9d
	68	14.7	37d
	32-176	14.7	84d
	100-600	38-1995[a]	22d
carbon dioxide	660-700	135-1330[a]	13d
	122-392	20-1330[a]	88d
	68-100	14.7	3d
	32-142	14.7	6d
	40-72	14.7	9d
	59.9	13.9	10d
	77	14.7	16d
	77	5-15	17d
	77	14.7	18d

Table 9-0.3 (Continued)

Gas	Temperature Range (°F)	Pressure Range (psia)	Reference
	59-77	14.7	20d
	77	14.7	26d
	75-81	22-51	40d
	65-79	14.7	45d
	53-170	1-14	49d
	77	14.7	50d
	32	14.7	56d
	77	14.7	59d
	59-115	10-17	61d
	32-140	14-440	87d
	68-100	14.7	67d
	32-140	14.7	85d
	68-95	370-1120	70d
	122-662	2300-51500	66d
	60-500	69-2912[a]	23d
sulfur dioxide	77	14.7	19d
	50-90	0-0.5	53d
	86-158	0.78-32[a]	4d
helium	220-530	50-145	54d
	32-122	14.7	2d
	100.4	14-90	31d
	36-86	14.7	68d
	32-122	14.7	85d
	40-164	14.7	44d
argon	32-122	14.7	2d
	32-122	14.7	68d
	32-122	14.7	85d
	51-160	14.7	44d
	77-550	54-430[a]	54d
	93-564	193-325[a]	12d
neon	32-122	14.7	2d
	48-165	14.7	44d
	71-519	235-344[a]	12d
	158-543	122-183[a]	54d

Table 9-0.3 (Continued)

Gas	Temperature Range (°F)	Pressure Range (psia)	Reference
krypton	141-482	220-393[a]	12d
	32-122	14.7	2d
	33-68	14.7	35d
	33-122	14.7	68d
	44-167	14.7	44d
xenon	142-398	94-539[a]	12d
	32-122	14.7	2d
	104-575	94-270	64d
	32-122	14.7	68d
	55-161	14.7	44d
nitrous oxide	46-75	14.7	28d
	77	14.7	38d
	38-76	14.7	58d
	77	14.7	59d
	32-68	14.7	85d
	50-77	14.7	20d
nitric oxide	32-176	14.7	84d
chlorine	50-77	0.8-14.7	76d
bromine	32-140	14.7	85d
iodine	68	14.7	32d
	32-223	14.7	69d

[a]Partial pressure

Table 9-0.4 – Literature Sources of Data for the Salt Effects on Solubility of Nonhydrocarbon Gases in Water

Gas	Salts	Temperature Range (°F)	Pressure Range (psia)	Reference
nitrogen	Na_2SO_4, Na_2SO_3	59, 77, 95	14.7[a]	232a
oxygen	LiCl, NaCl, KCl, RbCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$	--	--	156a
	Na_2SO_4	59, 77, 95	14.7[a]	232a
carbon monoxide	Sea water (natural and synthetic)	77	14.7	142a
carbon dioxide	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$	68-194	0.2-4.8[a]	31a
	Sea water, NaCl	33-86	14.7	126a
	NaCl, $CaCl_2$	77, 122, 167	735	131a
	LiCl, NaCl, NH_4NO_3, $BaCl_2$, Na_2SO_4, HNO_3, $CaCl_2$,			159a
	$Ca(NO_3)_2$, $NaHSO_3$, KI	77	14.7	198a
	CaO	387-1,110	300-21,000	205a
	Synthetic sea water	23-77	14.7-660	211a
	NaCl	302-842	1500-20,000	
hydrogen sulfide	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$	68-194	1-2[a]	31a
ammonia	NaCl, NH_4Cl	170-220	14.7	69a
	KOH	86-176	14.8[a]	103a
sulfur dioxide	K_2O	140, 158, 176, 194	2.6-9.9[a]	127a

Note: for a complete listing of literature sources of data for the salt effects on solubility of nonhydrocarbon gases in water, see the review articles by Markham and Kobe (132a), Battino and Clever (13a), and Wilhelm and Battino (226a, 227a). This table is an update of these review articles.

[a]Partial pressure.

Table 9-0.5 – Substances Forming Gas Hydrates

Structure I, All Cavities Filled Theoretical Composition M•5-3/4 H_2O		
argon	ethene	phosphine
krypton	ethyne	nitrous oxide
xenon	carbon dioxide	fluoromethane
nitrogen	carbon disulfide	difluoromethane
oxygen	carbonyl sulfide	trifluoromethane
methane	hydrogen sulfide	tetrafluoromethane
	hydrogen selenide	

Structure I, Small Cavities Empty Theoretical Composition M•7 2/3 H_2O	
chlorine	bromomethane
bromine	chloromethane
bromine chloride	chlorofluoromethane
chlorine dioxide	chlorodifluoromethane
sulfur dioxide	fluoroethane
arsine	fluoromethane
methyl mercaptan	ethylene oxide
ethane	cyclopropane

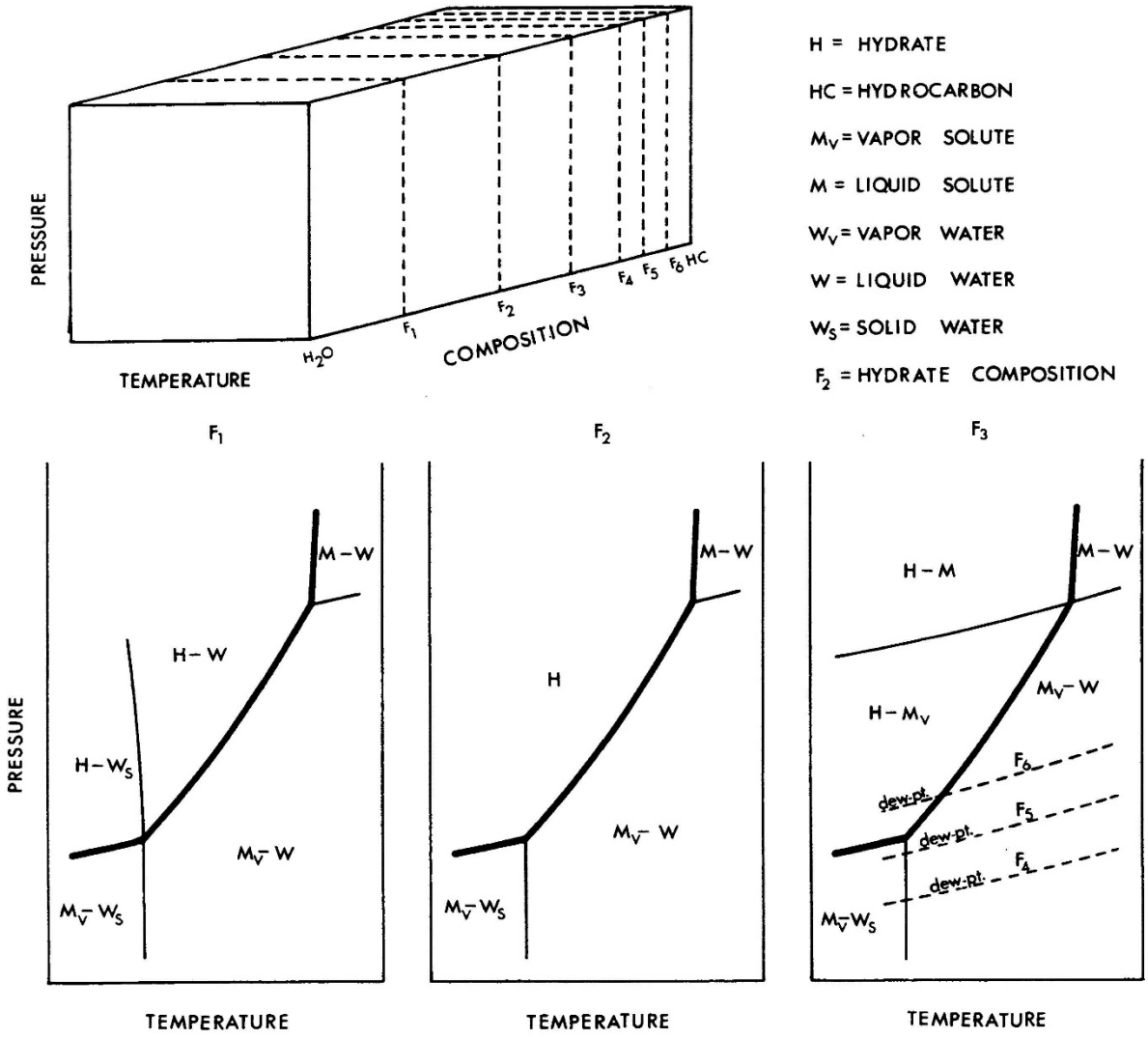
Structure II, Small Cavities Empty Theoretical Composition M•17 H_2O	
sulfur hexafluoride	1,2-dichloroethane
ethane	Iodomethane
propane	1,1-difluoroethane
propene	fluoroethene
cyclopropane	bromoethane
2-methylpropane	bromodifluoromethane
cyclopentane	bromotrifluoromethane
cyclopentene	dibromodifluoromethane
dimethyl ether	fluorodichloromethane
nitromethane	fluorotrichloromethane
dichloromethane	difluorodichloromethane
chloroform	1,1-difluoro-1-chloroethane
chloroethane	difluorobromochloromethane
1,1-dichloroethane	chloroethene

Note: From the tabulations in References 5b, 19b, 42b, 63b, 118b, 120b, 122b, 123b, 132b, 133b, 144b, 146b.

Table 9-0.6 – Substances Forming Gas Hydrates only When in the Presence of a Strong Hydrate Former (Help Gas)

System - Water, Help Gas, and	**Reference**
radon	86b, 87b
n-butane	76b
2-methylbutane	20b
cyclopentane	20b
methylcyclopentane	20b
benzene	123b
chloropicrin (trichloronitromethane)	123b
dimethyl sulfide (methylthiomethane)	123b
carbon tetrachloride (tetrachloromethane)	42b, 120b, 123b
trichlorobromomethane	42b, 123b
dibromomethane	42b
1,2-dichloroethane	42b, 123b
1,1,2-trichloroethane	42b
1,1,1,2-tetrachloroethane	42b
1,1,1-trifluoro-2-chloroethane	5b
bromoethane	42b, 120b
1,2-dibromoethane	42b
Iodoethane	42b
1,1-dichloroethene	42b
1,1,2-trichloroethene	42b
1,1,2-trifluoroethene	120b
bromoethene	42b
1,1-dibromoethene	42b
iodoethene	42b
1-chloropropane	42b
1-bromopropane	42b, 123b
2-bromopropane	42b
allyl chloride (3-chloropropene)	42b
allyl bromide (3-bromopropene)	42b
2-chlorobutane	42b
2-bromobutane	42b

Figure 9-0.7 – Gas Hydrate Phase Relations



Note: This figure is taken from Scauzillo (34c).

Table 9-0.8 – Literature Sources of Hydrate Equilibrium Data for Substances Occurring in Natural Gases

System - Water and	Reference
methane	30b, 31b, 54b, 55b, 59b, 64b, 70b,
	76b, 78b, 99b, 100b, 114b, 130b,
	131b, 144b
ethane	29b-31b, 54b, 55b, 59b, 98b-100b,130b
propane	29b-31b, 54b, 60b, 98b, 102b, 133b,
	144b, 145b
2-methylpropane (isobutane)	104b
cyclopropane	5b, 58b
ethene (ethylene)	23b, 33b, 34b, 98b, 114b, 130b,
	131b, 144b
propene (propylene)	98b
ethyne (acetylene)	130b, 137b, 144b
hydrogen sulfide	42b, 50b, 107b, 112b, 144b
carbon dioxide	30b, 31b, 54b, 102b, 128b, 144b
argon	7b, 78b, 144b
nitrogen	24b, 64b, 78b, 129b
oxygen	24b, 129b
sulfur dioxide	144b
krypton	7b, 144b
xenon	7b, 144b
methane-ethane	31b, 76b, 127b
methane-propane	18b, 31b, 76b, 127b, 148b
methane-n-butane	31 b, 76b
methane-2-methylpropane	31b, 76b, 83b, 127b
methane-ethene	114b
methane-propene	92b
methane-carbon dioxide	3 l b, 101b, 128b
methane-hydrogen sulfide	91b
methane-argon	62b, 105b
methane-krypton	62b
methane-nitrogen	64b
ethane-propane	31b,99b
ethane-ethene	73b
propane-ethene	40b
propane-2-methylpropane	38b
propane-propene	98b
propane-2-methyl-1-propene	38b
propane-hydrogen sulfide	97b

Table 9-0.8 (Continued)

System - Water and	Reference
propane-nitrogen	82b
propane-carbon dioxide	83b, 102b
ethene-propene	74b
nitrogen-argon	145b
methane-ethane-propane	31b, 59b
methane-propane-cs_2	127b
methane-hydrogen sulfide-carbon dioxide	101b
propane-propene-2-methylpropane	39b
propane-propene-2-methyl-1-propene	38b
propane-2-methylpropane-2-methyl-1-propene	38b
methane-ethane-propane-2-methylpropane	83b
propane-propene-n-butane-2-methylpropane	39b
propane-propene-2-methylpropane-2-methyl-1-propene	38b
methane-ethane-propane-n-butane-2-methylpropane	76b
methane-ethane-propane-nitrogen-n-butane	31b
methane-ethane-propane-2-methylpropane-hydrogen	83b
methane-ethane-propane-nitrogen-carbon dioxide	31b, 145b
methane-ethane-propane-n-butane-2-methylpropane-nitrogen-n-pentane	145b
methane-ethane-propane-nitrogen-carbon dioxide-n-butane	54b, 80b
methane-ethane-propane-2-methylpropane-nitrogen-n-butane-n-pentane	145b
methane-ethane-propane-hydrogen sulfide-nitrogen-carbon dioxide-n-butane	31b
natural gases	15b, 18b, 29b-31b, 35b, 54b, 80b, 106b, 110b, 126b, 145b

Figure 9-0.9 – Effect of Diethylene Glycol in Liquid-Phase Water on Conditions for Hydrate Formation in a Natural Gas of 0.595 Specific Gravity

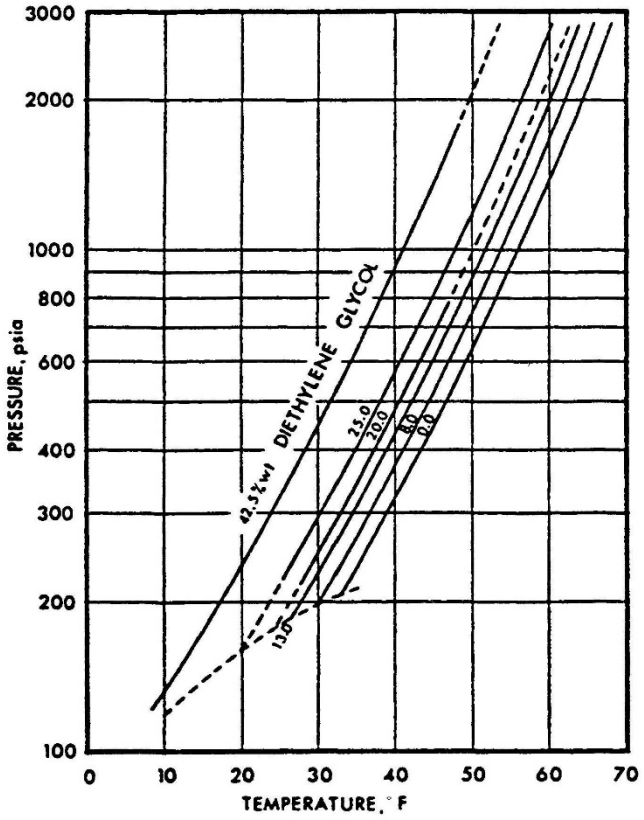
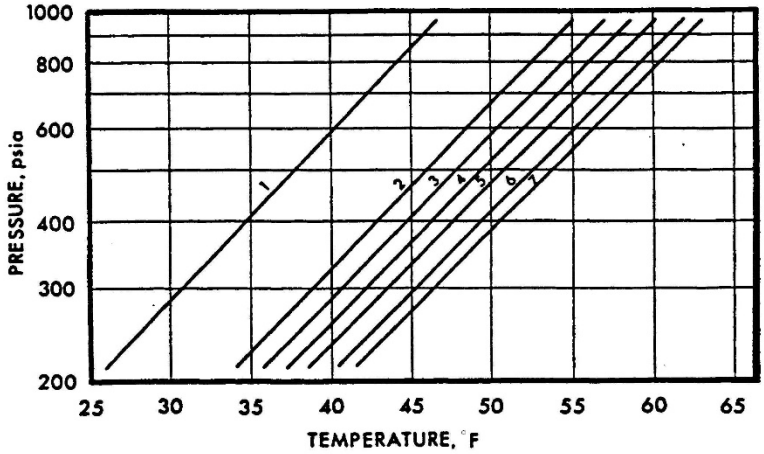


Figure 9-0.10 – Typical Effects of Dissolved Substances in Liquid-Phase Water on Hydrate Formation Conditions



Note: This figure is taken from Deaton and Frost (31b). The numbered curves represent 10-weight-percent aqueous solutions of the following: 1 = ammonia; 2 = methanol; 3 = ethanol or calcium chloride; 4 = propanol; 5 = ammonium bicarbonate; 6 = acetone; 7 = pure water.

Table 9-0.11 – Computer Methods

Procedure	Description
9A1.1	Solubility of Water in Pure Liquid Hydrocarbons Under Vapor-Liquid-Liquid Equilibrium Conditions
9A1.3	Solubility of Water in Undefined Liquid Hydrocarbon Mixtures
9A1.3	Solubility of Water in Undefined Liquid Hydrocarbon Mixtures
9A1.5	Solubility of Water in Pure Hydrocarbons and Hydrocarbon Mixtures
9A2.1	Solubility of Hydrocarbons in Water Under Vapor-Liquid-Liquid Equilibrium Conditions
9A2.3	Solubility of Solid, Polynuclear Aromatics in Water
9A2.6	Solubility of Hydrocarbons in Water under Vapor-Liquid-Liquid Equilibrium at 77 °F
9A3.1	Water Content of Natural Gases in Equilibrium with Liquid Water
9A6.1	(Flash) Modified Soave-Redlich-Kwong Equation of State for Phase Equilibrium Ca1culations for Water-Hydrocarbon Systems
9A7.1	Henry's Constants for Selected Gases in Water
9A7.3	Equilibrium Concentrations of Sour Gas Systems in Water
9A8.1	pH of Ammonia and Hydrogen Sulfide Gases in Water

9A Vapor-Liquid Equilibria in Systems Containing Water

9A1 Solubility of Water in Hydrocarbons

Procedure 9A1.1 – Solubility of Water in Pure Liquid Hydrocarbons under Vapor-Liquid-Liquid Equilibrium Conditions

Discussion

This procedure was last updated in 2005. The following equation is to be used to calculate the solubility of water in defined liquid hydrocarbons at P_3, the three-phase equilibrium pressure (that is, under vapor-liquid-liquid equilibrium conditions) or at slightly higher pressures (where there is no vapor phase but the solubility of water is essentially the same as that at P_3).

$$ln(x_w) = a_1 + a_2/T \qquad (9A1.1\text{-}1)$$

Where:

x_w	=	*mole fraction of water in the hydrocarbon-rich liquid phase*
a_1, a_2	=	*component-specific parameters (see Table 9A1.2)*
T	=	*absolute temperature, in °R*

Table 9A1.2 also includes the temperature range (in °F) of the data for each hydrocarbon used in the regression with Equation (9A1.1-1); the number of data points and their sources; the percent AAD (average absolute deviation) and bias (a positive bias indicates that the calculated values are, on average, higher than the experimental); and two properties of the three-phase critical end point: T_{3c} (the maximum temperature at which the hydrocarbon-rich liquid phase can exist) and $x_{w,3c}$ (with reference) and the calculated $x_{w,3c}$. Because of an upward inflection in the solubility as T_{3c} is approached (an inflection that becomes steeper and wider as the carbon number increases), the $x_{w,3c}$ calculated with Equation (9A1.1-1) is significantly lower than the experimental value, especially for carbon numbers greater than 5.

Procedure

Step 1: Read the parameters a_1 and a_2 for the given hydrocarbon from Table 9A1.2.

Step 2: Calculate the solubility with Equation (9A1.1-1).

Comments on Procedure 9A1.1

Purpose

This procedure calculates the solubility of water in defined liquid hydrocarbons over the temperature range given for each hydrocarbon in Table 9A1.2.

Limitations

The valid temperature range for each hydrocarbon is given in Table 9A1.2. Limited extrapolation outside these ranges is acceptable, subject to the following considerations. Below 32 °F, the stable phase of water is solid, but the change in phase is likely to have only a small effect on the solubility if the extrapolation is not much more than about 10 °F. Extrapolation to within approximately100 °F of T_{3c} is generally permissible. If it is desired to calculate x_w up to T_{3c}, it will be necessary to use a more complex equation, such as Equation 6 in reference (88a).

Equation (9A1.1-1) is applicable at P_3, the three-phase equilibrium pressure, where the vapor, hydrocarbon-rich liquid, and aqueous phases are in equilibrium. However, because the effect of pressure on the solubility of water in the hydrocarbon-rich liquid is very small, the solubility at pressures moderately higher than P_3 (where there is no vapor phase) will essentially be equal to that calculated with Equation (9A1.1-1). As an example, in the case of the solubility of water in benzene, the data of Thompson and Snyder (214a) at 100 °F show a 10 percent *decrease* in solubility as the pressure is raised from 1000 psig to 5000 psig. If $P < P_3$, then we have equilibrium between the vapor and the hydrocarbon-rich liquid, where pressure can have a significant effect on the liquid mole fraction of water. For this situation, consult the original data sources listed in Table 9-0.2.

The solubility of water in a given family of hydrocarbons is relatively insensitive to the hydrocarbon's structure. For example, the solubility in a branched alkane is within 10 % of that in a normal alkane of the same carbon number; the same is also true when the solubility of water in xylenes is compared to that in ethylbenzene. Thus, the parameters a_1 and a_2 in Table 9A1.2 can be used to estimate the solubility of water in a hydrocarbon of the *same family and carbon number*.

Reliability

Generally, the average absolute deviation of solubilities calculated with Equation (9A1.1-1) is around 10 percent. However, the AAD from data that are considered to be of poor quality can be much greater. For example, in the case of the solubility of water in *n*-butane, the AAD of the calculated values from selected data was approximately 7 percent, but from the discarded data of Black et al. (18a) it was *85 percent*.

Literature Sources

The parameters listed in Table 9A1.2 were regressed from the data in the references given in the table. See also (280a, 281a). Additional references may be found in Table 9-0.2.

Example

Calculate the solubility of water in benzene at 104 °F under vapor-liquid-liquid equilibrium.

From Table 9A1.2, the appropriate parameters are $a_1 = 5.01662$ and $a_2 = –5808.44$. The temperature is 104 + 459.67 = 563.67 °R. Substituting into Equation (9A1.1-1), the calculated x_w

value is 5.05×10^{-3}. Experimental solubilities at 104 °F that were used in the regression ranged between 4.48×10^{-3} and 5.08×10^{-3}. As an example of a value from a reference that was discarded, Englin et al. (56a) reported 4.10×10^{-3}.

Table 9A1.2 – Parameters for Equation (9A1.1-1): Solubility of Water in Hydrocarbons

	a_1	a_2	T Range/°F	Data Sources		%AAD	%Bias	t(3C)/°F	ref	X(w,3c)	
				# Points	References					exp(ref)	calc
Normal Alkanes											
propane	7.84827	-8477.57	32 – 202	25	109a, 275a, 276a	5.70	0.26	205.7	109a	0.00998(109a)	0.0075
butane	7.34412	-8115.26	77 – 300	13	176a, 223a, soly. at 77 F with Eq. 5 (280a)	6.85	-0.19	305.6	176a	0.0483(176a)	0.0384
pentane	6.95193	-7886.46	32 – 302	7	18a, 67a, 169a	7.81	1.89	376.1	230a	0.187(230a)	0.0834
hexane[a]	6.69807	-7724.13	32 – 392	9	30a, 169a, 183a, 216a, 278a	8.49	0.49	431.5	230a	0.342(230a)	0.140
heptane[b]	6.76126	-7723.26	32 – 122		See Figure 7 in 280a.			476.3	242a		
octane	6.83937	-7722.3	32 – 464	9	30a, 88a, 169a, 278a See Figure 6 in 280a.	6.76	0.40	510.7	88a	0.527(88a)	0.327
nonane[b]	6.67868	-7622.51	77	1	192a			537.5	242a		
decane	6.47656	-7522.73	77 – 482	12	78a, 192a, 254a, 278a	9.75	0.63	560.4	254a	0.706(254a)	0.407
hexadecane	6.41816	-7360.91	77 – 572	5	192a, 278a	2.86	0.08	635.3	242a		
Normal Alkylcyclohexanes											
cyclohexane	6.52382	-7793.64	50 – 470	20	70a, 72a, 107a, 178a, 183a, 216a, 255a	10.44	1.18	491.1	230a	0.384(230a)	0.188
methylcyclohexane[c]	6.61534	-7793.64	40 – 500	12	56a, 78a, 153a, 273a	43.54	-7.77	520	184a		
ethylcyclohexane	6.73185	-7793.64	100 – 535	6	88a	7.59	-7.18	550.8	88a	0.603(88a)	0.375
butylcyclohexane	6.74601	-7793.64	100 – 530	8	254a, 273a	7.26	0.05	592.1	254a	0.750(254a)	0.515
Linear 1-Alkenes											
propene	6.61939	-7144.16	32 – 106	9	64a, 275a	8.75	0.94	197.9	125a	0.0096(125a)	0.0143
1-butene	6.44349	-7144.16	100 – 280	8	124a, 223a	7.53	5.14	297	124a	0.0514(124a)	0.0499
1-hexene[a]	6.62134	-7360.66	100 – 396	4	254a	5.25	0.16	428.3	254a	0.312(254a)	0.189
1-octene	6.59697	-7360.66	100 – 500	5	254a	12.92	-4.62	510.9	254a	0.517(254a)	0.373
1-decene	6.50659	-7360.66	214 – 396	3	254a	6.13	-3.25	564.5	254a	0.700(254a)	0.506

Table 9A1.2 – Continued

	a_1	a_2	T Range/°F	Data Sources		%AAD	%Bias	t(3C)/°F	ref	X(w,3c)	
				# Points	References					exp(ref)	calc
1,3-Butadiene	4.08105	-5491.82	32 – 140		fit of curve in 238a	0.88	0.01				
Alkylbenzenes											
benzene[a]	5.01662	-5808.44	42 – 437	126	In addition to refs. in 199a, 216a: 3a, 244a, 245a, 277a	5.92	0.32	516.8	230a	0.555(230a)	0.394
toluene[a]	5.00877	-5888.88	32 – 482	57	In addition to refs. in 199a: 3a, 244a, 246a, 273a	14.10	3.93	545	184a		
ethylbenzene[a]	4.91089	-5879.85	32 – 505	18	56a, 88a, 169a, 247a	12.83	1.14	562.9	88a	0.691(88a)	0.432
1,3,5-trimethylbenzene	4.26359	-5583.85	68 – 212	11	56a, 247a	3.76	0.10				
Ethenylbenzene (styrene)	4.16630	-5262.58	43 – 124	10	119a	5.52	0.22				
Multiring Hydrocarbons											
cis-decalin	5.29501	-6793.14	68 – 577	9	56a, 78a, 254a	12.35	1.03	618.7	254a	0.791(254a)	0.366
tetralin	5.72195	-6597.17	214 – 577	5	248a, 254a	13.91	1.15	613.0	254a	0.939(254a)	0.652
1-methylnaphthalene	4.87811	-5625.86	32 – 572	13	56a, 248a, 254a	11.41	0.89	601.3	254a	0.922(254a)	0.597
1-ethylnaphthalene	4.75428	-5665.16	100 – 530	6	254a	4.92	0.14	610.3	254a	0.927(254a)	0.583
x-terphenyl	3.80410	-4573.69	200 – 575	9	263a	3.51	0.09				

[a] Additional data have been reported for the solubility of water in n-hexane (240a), 1-hexene (272a), benzene (259a, 272a), toluene (241a, 259a), and p-xylene (259a). The parameters for ethylbenzene reproduce the new data in p-xylene to within 13% but they are within 5% of earlier data in the three xylenes (56a, 169a, 247a).

[b] The parameters for heptane and nonane were interpolated as described in (280a): the solubility at 77 °F was calculated with Eq. (5); and the value of the parameter a_2 was interpolated between those of hexane and octane (for heptane), and of octane and decane (for nonane).

[c] Parameter a_1 for methylcyclohexane was determined by substituting into Eq. (9A1.1-1) the solubility of water at 77 °F – which was calculated with Eq. (8) of (281a). The parameter a_2 is the same for all alkylcyclohexanes.

Procedure 9A1.3 – Solubility of Water in Undefined Liquid Hydrocarbon Mixtures

Discussion

This procedure was last updated in 2005. The following equation is to be used to calculate the solubility of water in undefined liquid hydrocarbon mixtures at P_3, the three-phase equilibrium pressure (that is, under vapor-liquid-liquid equilibrium conditions) or at slightly higher pressures (where there is no vapor phase but the solubility of water is essentially the same as that at P_3).

$$ln(x_w) = a_1 + a_2/T \qquad (9A1.3\text{-}1)$$

Where:

x_w	=	*mole fraction of water in the undefined liquid hydrocarbon mixture*
a_1, a_2	=	*component-specific parameters (see Table 9A1.4)*
T	=	*absolute temperature in °R*

Table 9A1.4 also includes available characterization properties of the undefined hydrocarbon mixture (API gravity, molecular weight and Watson characterization factor); the temperature range (in °F) of the data used in the regression with Equation (9A1.3-1); the number of data points and their sources; and finally, the percent AAD (average absolute deviation) and bias (a positive bias indicates that the calculated values are, on average, higher than the experimental).

Procedure

Step 1: *Read the parameters a_1 and a_2 for the given undefined hydrocarbon mixture from Table 9A1.4.*

Step 2: *Calculate the solubility with Equation (9A1.3-1).*

Comments on Procedure 9A1.3

Purpose

This procedure calculates the solubility of water in selected undefined liquid hydrocarbon mixtures over the temperature range given for each compound in Table 9A1.4.

Limitations

The valid temperature range for each hydrocarbon is given in Table 9A1.4. Limited extrapolation outside these ranges is acceptable, subject to the following considerations. Below 32 °F, the stable phase of water is solid but the change in phase is likely to have only a small effect on the solubility if the extrapolation is not much more than about 10 °F. Extrapolation to higher temperatures is generally permissible to about 100 °F below T_{3c}, the three-phase critical end point temperature (the highest temperature at which the hydrocarbon-rich liquid phase can exist). If T_{3c} is not known, an estimate can be made by figuring out which pure hydrocarbon approximates the properties of the undefined mixture (see the following section).

Equation (9A1.3-1) is applicable at P_3, the three-phase equilibrium pressure, where the vapor, hydrocarbon-rich liquid and aqueous phases are in equilibrium. However, since the effect of pressure on the solubility of water in the hydrocarbon-rich liquid is very small, the solubility at pressures moderately higher than P_3 (where there is no vapor phase) will essentially be equal to that calculated with Equation (9A1.3-1). (See also the discussions on Limitations of Procedure 9A1.1.) If $P < P_3$, then we have equilibrium between the vapor and the hydrocarbon-rich liquid, where pressure can have a significant effect on the mole fraction of liquid water. For this situation, consult the original data sources listed in Table 9-0.2.

Relationship between Undefined Hydrocarbon Mixtures and Defined Hydrocarbons

The available characterization information for the undefined liquid hydrocarbon mixtures provides some information on the relative amounts of paraffins and aromatics in that mixture. For example, the properties of the naphtha cut are similar to those of *n*-decane; the lube oil is close to a C_{30} paraffin; and the water solubility in the aromatic coal solvent is well represented by that in 1-methylnaphthalene. As shown in Table 9A1.4, a single set of parameters fits the data for the solubility of water in the two kerosene samples (75a, 76a), and another set fits the data in the lube oil (75a) *and* the paraffin oil (76a). Furthermore, the fit of the solubility data provides another check because the parameter a_2 is related to the heat of solution ($a_2 = -H_{sol}/R$). Thus, the absolute value of a_2 is about 7500 for paraffins and naphthenes but is generally under 6000 for aromatics (except in the vicinity of T_{3c}, where the solubility curve becomes very steep). This can be very useful in screening solubility data.

Reliability

Although the average absolute deviation of solubilities calculated with Equation (9A1.3-1) is less than 10 percent (see Table 9A1.4), this is true only for the undefined mixtures given in the table.

Several pre-1950 sources report data for the solubility of water in aviation gasolines. Most of these data were obtained at or near room temperature, frequently at a single temperature. The data scatter is substantial which is only partly due to differences in the makeup of the gasolines. As an example, Aldrich (1a) measured the solubility of water in 5 aviation gasolines at 50 to 122 °F. Two of the fuels, No. 10 and No. 19, were essentially identical: they were mostly paraffinic and had mid-NBP's of 147 and 149 °F and specific gravities of 0.68. Yet, Aldrich reported that the solubility of water in Fuel 10 was about *3 times higher* than that in Fuel 19. Furthermore, the reported increase in solubility with temperature (or the heat of solution) for both fuels was *much* smaller than that in the corresponding paraffin (3-methylpentane: NBP at 146 °F; S = 0.669)—or any other paraffin or naphthene. The same criticism can be made for the water solubility data in JP-3 fuel (114a) and JP-4 fuel (40a) which also scatter widely.

Literature Sources

The parameters listed in Table 9A1.4 were regressed from the data in the references given in Table 9A1.4. Additional references may be found in Table 9-0.2.

Example 1

Calculate the solubility of water in a lube oil (75a) at 419 °F under vapor-liquid-liquid equilibrium.

From Table 9A1.4, the appropriate parameters are a_1 = 6.33472 and a_2 = –7164.85. The temperature is 419 + 459.67 = 878.67 °R. Substituting into Equation (9A1.3-1), the calculated x_w value is 0.162.

Griswold and Kasch (75a) report two experimental solubilities at 419 °F: 0.173 and 0.183.

Example 2

Calculate the solubility of water at 77 °F in a motor gasoline that contains 60 mole % paraffins,5 mole % olefins, 5 mole % naphthenes and 30 mole % aromatics. The gasoline's average carbon number is 7.

Since the PONA analysis is known, the solubility of water in motor gasoline can be estimated using the relationship

$$ln(x_{w,m}) = \sum x_i^{hc}\left[ln(x_{w,i})\right] \qquad (9A1.3\text{-}2)$$

Where:

$x_{w,m}$	=	*the solubility of water in the mixture*
x_i^{hc}	=	*the mole fraction of the hydrocarbon component i in the water-free mixture*
$x_{w,i}$	=	*the solubility of water in the (pure) hydrocarbon component i*

Since the average CN of the gasoline is 7, its components can be represented by heptane, heptene, methyl-cyclohexane and toluene. Substituting the solubilities calculated with Equation (9A1.1-1) and the parameters in Table 9A1.2 into Equation (9A1.3-2), we have:

$$ln(x_{w,m}) = (0.60)\, ln(4.857 \times 10^{-4}) + (0.05)\, ln(8.20 \times 10^{-4}) + (0.05)\, ln(3.682 \times 10^{-4}) + (0.30)\, ln(2.569 \times 10^{-3})$$

$$x_{w,m} = 8.11 \times 10{-}4$$

Thus, due to the presence of 5 mol % olefins and, especially, 30 mol % aromatics, the solubility of water in this gasoline is 70 % higher than that in heptane. The a_1 parameter for water in heptene was set equal to the average of the a_1 parameters for hexene and octene.

Table 9A1.4 – Parameters for Equation (9A1.3-1): Solubility of Water in Undefined Liquid Hydrocarbon Mixtures

Undefined Mixture		Gravity (°API)	MW	Watson Characterization Factor [a]	a_1	a_2	T Range/ °F	Data Sources		% AAD	% Bias
								# Points	References		
aviation gasoline[b]		70.6	95	12.2	6.31813	-7502.64	32 – 100	9	37a, 239a	9.99	0.66
naphtha		54.2	147	12.2	6.28057	-7208.1	318 – 432	4	75a	1.51	0.02
kerosene	(75a)	41.9	173	11.8	6.22015	-7238.69	64 – 507	23	75a, 76a	8.50	0.48
kerosene	(76a)	47.1	170	12.0							
lube oil	(75a)	29.3	434	12.4	6.33472	-7164.85	61 – 538	22	75a, 76a	5.48	0.25
paraffin oil	(76a)	28.8	350	12.1							
diesel fuel dz[c]		37.0	200	11.7	8.27790	-9210.76	392 – 623	7	256a	4.60	0.14
heavy diesel fuel[c]		38.2	200	11.8	7.67509	-8619.48	392-631	6	256a	5.04	0.19
diesel fuel ds[c]		39.2	226	12.0	7.46718	-8394.75	392 – 639	6	256a	1.78	0.03
hydroisomerizate[c]		40.6	187	11.9	8.13573	-9033.24	392 – 622	7	256a	4.48	0.13
wide petroleum cut[c]		36.0	253	12.4	7.10396	-8109.52	482 – 660	6	256a	3.43	0.12
coal solvent		14.4	187	10.0	4.18192	-5182.69	104 – 392	3	282a	8.22	0.50

[a] Watson Characterization factor, K = (MeABP/ °R)^(1/3) / S, where S (specific gravity at 60/60 °F) = 141.5/(°API + 131.5).

[b] Straight-run product: gravity = 0.70; IBP = 104 °F, Dry Point = 293 °F (249a).

[c] The rate of the solubility increase with temperature is very steep, which is characteristic of the shape of the solubility curve as it approaches the tricritical point (which is the upper end of the temperature range for each cut).

Procedure 9A1.5 – Solubility of Water in Pure Hydrocarbons and Hydrocarbon Mixtures

Discussion

This procedure was last updated in 2005. The following equation is to be used to predict the solubility of water in pure hydrocarbons or in hydrocarbon mixtures when these data cannot be obtained from Procedure 9A1.1 or 9A1.3.

$$\log x_w = -\left(4200\frac{H}{C} + 1050\right)\left(\frac{1.8}{T} - 0.0016\right) \qquad (9A1.5\text{-}1)$$

Where:

x_w	=	*soluble mole fraction of water in hydrocarbon*
H/C	=	*weight ratio of hydrogen to carbon in hydrocarbon*
T	=	*absolute temperature, in °R*

Procedure

Step 1: *For pure hydrocarbons, calculate the hydrogen-to-carbon ratio. For hydrocarbon mixtures of undefined composition, this ratio may be determined using Figure 2B6.1.*

Step 2: *Calculate the mole fraction solubility of water using Equation (9A1.5-1) with the appropriate ratio and temperature.*

Comments on Procedure 9A1.5

Purpose

This procedure predicts the solubility of water in defined hydrocarbons and undefined hydrocarbon mixtures as a function of the weight ratio of hydrogen to carbon of the hydrocarbon.

Limitations

Equation (9A1.5-1) generally can be used from 32 °F up to about 100 °F below T_{3c}, the three-phase critical end point temperature (the highest temperature at which the hydrocarbon-rich liquid phase can exist); see also the Limitations of Procedures 9A1.1 and 9A1.3 with regard to the pressure range of applicability.

Equation (9A1.5-1), the Hibbard-Schalla correlation, does remarkably well for alkanes, alkenes heavier than C_3, and alkylbenzenes, including styrene. On the other hand, it does very poorly for alkylcyclohexanes and *cis*-decalin—and not too well for tetralin and alkylnaphthalenes. Since the largest deviations are for compounds having a cyclohexyl ring, it is reasonable to consider a modification of the Hibbard-Schalla correlation only for alkylcyclohexanes and, more generally, cycloalkanes or naphthenes—and possibly for naphtheno-aromatics.

Modification of Equation (9A1.5-1) for Naphthenic Rings

Water is slightly less soluble in a naphthene (C_nH_{2n}) than in the corresponding paraffin (C_nH_{2n+2}); see Figure 8 in (281a). However, Equation (9A1.5-1) predicts that water is *more* soluble in a naphthene than in a paraffin—and is independent of the carbon number. It follows, therefore, that the prediction of water solubility in a naphthene can be improved by adjusting its atomic formula so that there will be more than (2n + 2) H atoms for *n* C atoms. When the three alkylcyclohexanes (see Table 9A1.2) were given the arbitrary atomic formula C_nH_{2n+4}, the AAD (average absolute deviation) of water solubility *dropped from 96.5 % to 14.7 %.*

In the case of *cis*-decalin and tetralin, part of the deviation may be due to the questionable quality of the experimental data at high temperatures (254a). When the atomic formula of *cis*-decalin (and alkyldecalins) was adjusted from C_nH_{2n-2} to C_nH_{2n+2}, representing an addition of 4 H atoms, the AAD was cut from 93.2 % to 48.5 %. By analogy, only 2 H atoms were added to tetralin, and thus its atomic formula (and that of alkyltetralins) became C_nH_{2n-6}, which led to a reduction of the AAD from 35.2 % to 23.7 %.

The adjustments in the atomic formulas for compounds containing cyclohexyl rings improve the overall reliability of the Hibbard-Schalla correlation but this improvement cannot be confirmed for other naphthenes. Comparison of Equation (9A1.5-1) against the generally unreliable data of Englin et al. (56a) for alkylcyclopentanes (the only other naphthenes for which information for the solubility of water is available) gave a smaller AAD than for alkylcyclohexanes and a bias that was positive for cyclopentane but gradually turned negative (solubility was underpredicted) for higher carbon numbers.

Two alternatives to the Hibbard-Schalla correlation are discussed in the following section.

Two Alternatives to Equation (9A1.5-1)

Grant Wilson proposed in reference (22a) a graphical correlation for the solubility of water as a function of the “double bond index”

$$DBI = 2n_D/n_C$$

Where:

n_D = *the number of double bonds*

n_C = *the number of carbon atoms (CN) in the hydrocarbon*

Although the graphical DBI correlation appears reasonable for olefins and aromatics, it suffers from a significant limitation. It predicts, at a given temperature, *the same solubility for* **all** *paraffins and naphthenes*; that is, it does not predict a lower solubility in naphthenes or an increasing solubility of water with increasing n_C.

Another generalization was recommended in references (280a, 281a), especially for defined hydrocarbons and mixtures of defined hydrocarbons that is based on Equation (9A1.1-1). When its parameters a_1 and a_2 are not available for a hydrocarbon, generalized procedures for the heat of solution and the solubility of water at 77 °F can provide very useful estimates:

$$a_2 = -H_{sol}/R$$

$$a_1 = ln(x_w)_{T^*} - a_2/T^*$$

Equation (9A1.1-1) results from the assumption that H_{sol}, the heat of solution, is constant. It follows that, if we can measure H_{sol} and the solubility of water at a single temperature T*, which conveniently can be (77 + 459.67) °R, we can determine the two parameters and can thus predict the water solubility as a function of temperature. Furthermore, the near constancy of H_{sol} for each family helps in screening questionable data. (R is the gas constant, 1.9859 Btu per (lbmol) (°R).

Reference (281a) provides reliable estimates for the heat of solution (on page 199 therein), while the solubility of water at 77 °F is given by Equation 8 and the parameters in Table 2 (on page 197).

Reliability

Except for propene and hydrocarbons with naphthenic rings, the average absolute deviation of water solubilities in defined hydrocarbons calculated with Equation (9A1.5-1) is generally less than 20 percent.

Literature Source

Equation (9A1.5-1) was developed by Hibbard and Schalla, *Natl. Advisory Comm. Aeron*. RM E 52024 (1952).

Examples

A. Find the solubility of water in isopentane at 68°F.

The atomic weights of hydrogen and carbon are 1.008 and 12.01, respectively. The hydrogen-to-carbon weight ratio is:

$$\frac{(12)(1.008)}{(5)(12.01)} = 0.2014$$

The solubility is calculated using equation (9A1.5-1):

$$log(x_w) = -[(4200)(0.2014) + 1050]\left[\frac{1.8}{68 + 459.67} - 0.0016\right] = -3.429$$

x_w= *0.000368 mole fraction (solubility of water)*

An experimental run gave a solubility of water equal to 0.000376 mole fraction (18a).

B. Find the solubility of water at 255 °F in a lubricating oil having a 29.3 degree API gravity and a mean average boiling point of 765 °F.

The carbon-to-hydrogen weight ratio obtained from Chapter 2 is 6.6 and using equation (9A1.5-1):

$$log(x_w) = -\left(4200\frac{1}{6.6} + 1050\right)\left(\frac{1.8}{255 + 459.67} - 0.0016\right)$$

xw = 0.0282 mole fraction.

An experimental run gave a solubility of water equal to 0.0252 mole fraction (75a).

9A2 Solubility of Hydrocarbons in Water

Procedure 9A2.1 – Solubility of Hydrocarbons in Water under Vapor-Liquid-Liquid Equilibrium Conditions

Discussion

This procedure was last updated in 2005. The following equation is to be used to calculate the solubility of defined liquid hydrocarbons in water at P_3, the three-phase equilibrium pressure (that is, under vapor-liquid-liquid equilibrium conditions) or at slightly higher pressures (where there is no vapor phase but the solubility of water is essentially the same as that at P_3).

$$ln(x_{hc}) = a_1 + a_2/T + a_3\, ln(T) \qquad (9A2.1\text{-}1)$$

Where:

x_{hc}	=	*mole fraction of hydrocarbon in the water-rich liquid phase*
a_1, a_2, a_3	=	*component-specific parameters (see Table 9A2.2)*
T	=	*absolute temperature in °R*

Table 9A2.2 also includes the temperature range (in °F) of the data for each hydrocarbon used in the regression with Equation (9A2.1-1); the number of data points and their sources; the percent AAD (average absolute deviation) and bias (a positive bias indicates that on average the calculated values are higher than the experimental) and the *calculated* solubility at 77 °F.

Procedure

Step 1: *Read the parameters a_1, a_2, and a_3 for the given hydrocarbon from Table 9A2.2.*

Step 2: *Calculate the solubility with Equation (9A2.1-1).*

Comments on Procedure 9A2.1

Purpose

This procedure calculates the solubility of defined liquid hydrocarbons in water over the temperature range given for each hydrocarbon in Table 9A2.2.

Limitations

The valid temperature range for each hydrocarbon is given in Table 9A2.2. If needed, extrapolation down to 32 °F and up to 300 °F (the maximum temperature of interest in water pollution abatement in petroleum refineries) is generally permissible.

Equation (9A2.1-1) is applicable at P_3, the three-phase equilibrium pressure where the vapor, hydrocarbon-rich liquid and aqueous phases are in equilibrium. However, because the effect of pressure on the solubility of water in the hydrocarbon-rich liquid is very small, the solubility at pressures moderately higher than P_3 (where there is no vapor phase) will be only slightly *higher* than that calculated with Equation (9A2.1-1). (In the case of the solubility of water in a hydrocarbon, raising the pressure above P_3 leads to a *decrease* in the solubility.) If $P < P_3$, then we have equilibrium between the vapor and the hydrocarbon-rich liquid, where pressure can have a significant effect on the liquid mole fraction of water. For this situation, consult the original data sources listed in Table 9-0.2.

The solubility of members of a hydrocarbon family in water drops steeply with increasing CN (carbon number). Furthermore, for a given CN, branching increases the solubility relative to that of a normal isomer and this enhancement is proportional to the extent of branching. The solubility of dimethylbenzenes (xylenes) at 77 °F is within 10 % of that of ethylbenzene but only the 1,2-isomer is more soluble than ethylbenzene (see Table 9A2.2).

Generalized Correlations

Grant Wilson proposed in (22a) an approximate generalized correlation for the solubility of liquid hydrocarbons in water, x_{hc}:

$$log_{10}(x_{hc}) = -814.7/T + (0.271 - 289.96/T)(CN) - (1.533 - 1402.1/T)(HCT) \qquad (9A2.1\text{-}2)$$

T is the absolute temperature in Kelvin and HCT is a constant characteristic of each hydrocarbon type: HCT = 0 for alkanes (paraffins), 0.348 for alkenes (olefins), 0.333 for cycloalkanes (naphthenes), 1 for alkylbenzenes, and 1.385 for alkylnaphthalenes.

Equation (9A2.1-2) works “fairly well within the 200 °F to 400 °F range, but it quickly diverges from actual behavior outside of this range” (22a). It does not work well even in the claimed range of applicability, because the predicted curve for $\log(x_{hc})$ versus T is concave down while it is expected be concave up.

Another generalization that is based on Equation (9A2.1-1) was proposed in references (280a, 281a). When the parameters a_1, a_2, and a_3 are not available for a hydrocarbon, the following generalized procedures can provide useful estimates:

$a_3 = C_{p,sol} / R$

$a_2 = a_3 \times T_{min}$

$$a_1 = \ln(x_{hc})_{T^*} - a_2 / T^* - a_3 \ln(T^*)$$

Equation (9A2.1-1) results from the assumption that $C_{p,sol}$, the heat capacity of solution, is constant. It follows that H_{sol} (heat of solution) is a linear function of temperature. Generally, H_{sol} is negative below room temperature and goes through 0 at T_{min}, the temperature where the hydrocarbon solubility assumes its minimum value. T_{min} can be determined reliably if H_{sol} is measured calorimetrically (or the hydrocarbon solubility is measured carefully over the range, say, (32 to 120) °F). Furthermore, if the hydrocarbon solubility is known at a single temperature T*, which conveniently can be (77 + 459.67) °R, we can determine the three parameters and can thus predict the hydrocarbon solubility as a function of temperature. Furthermore, the near constancy of $C_{p,sol}$ and T_{min} for each family helps in screening questionable data. (R is the gas constant, 1.9859 Btu/ lb-mole ˚R.)

Reference (281a) provides recommendations for $C_{p,sol}$ and T_{min} in Section 3.3 (and Figure 5). The solubility of hydrocarbons in water at 77 °F is given in Table 9A2.2. These values can be extrapolated by plotting $\log(x_{hc})$ versus T or by using Equation (1) in 280a for normal alkanes; and Equations (1 - 3) in (281a) for, respectively, normal alkylbenzenes, normal alkylcyclohexanes (which is approximate), and linear 1-alkenes.

Reliability

Generally, the data scatter, even for selected data, is larger for the solubility of hydrocarbons in water than that of water in hydrocarbons. The average absolute deviation of solubilities calculated with Equation. (9A2.1-1) is less than 20 percent for most hydrocarbons in Table 9A2.2. However, the AAD from poor quality data can be much greater.

Literature Sources

The parameters listed in Table 9A2.2 were regressed from the data in the references given in the table. See also (280a, 281a). Additional references may be found in Table 9-0.2.

Example

Calculate the solubility of hexane in water at 212 °F under vapor-liquid-liquid equilibrium.

From Table 9A2.2, the appropriate parameters are $a_1 = -406.5873$, $a_2 = 29388.83$, and $a_3 = 53.89582$. The temperature is 212 + 459.67 = 671.67 °R. Substituting into Equation (9A2.1-1), the calculated x_{hc} value is 6.25×10^{-6}.

An experimental solubility at 212 °F that was used in the regression is 6.21×10^{-6} (216a). Two recent sources (240a, 265a) report at approximately 212 °F the value 6.16×10^{-6}.

Table 9A2.2 – Parameters for Equation (9A2.1-1): Solubility of Liquid Hydrocarbons in Water

Compound	a_1	a_2	a_3	T Range/ °F	Data Sources # Points	Data Sources References	% AAD	% Bias	xhc @ 77 °F
Normal Alkanes									
propane	-314.3825	24225.156	41.50287	54 – 205	15	109a	1.63	0.02	2.29E-04
butane	-292.4358	21452.230	38.58148	100 – 280	10	121a, 223a	5.79	0.22	4.71E-05
pentane	-361.7959	26167.450	47.97436	32 – 356	27	67a, 199a, 258a	10.91 [a]	3.50	1.01E-05
hexane	-406.5873	29388.830	53.89582	59 – 392	23	98a, 216a, 240a, 265a	10.02	0.28	2.11E-06
heptane	-430.4197	31018.136	56.95927	32 – 339	24	199a, 265a	13.82	-3.28	4.51E-07
octane	-344.6741	22519.372	45.60046	59 – 535	25	88a, 98a, 265a	9.43	0.75	1.02E-07
nonane [b]	-469.366	33782.08	61.940	59 – 77	3	98a, 269a	7.55	7.03	3.74E-08
Branched Alkanes									
monomethyl isomers	Multiply solubility of corresponding normal alkane at 77 °F by 1.3								
dimethyl isomers	Multiply solubility of corresponding normal alkane at 77 °F by 2.0								
trimethl isomers	Multiply solubility of corresponding normal alkane at 77 °F by 2.7								
cyclopentane	-235.6808	16843.48	30.89572	77 – 308	8	136a, 171a	2.65	0.07	4.09E-05

Table 9A2.2 – Continued

Compound	a_1	a_2	a_3	T Range/ °F	Data Sources # Points	Data Sources References	% AAD	% Bias	xhc @ 77 °F
Normal Alkylcyclohexanes									
cyclohexane	-326.8160	23264.01	43.2980	34 – 408 [c]	26	199a (low-T data), 216a, 250a, 264a	12.60 [d]	2.33	1.21E-05
methylcyclohexane	-356.3349	25331.92	47.1467	77 – 339	17	171a, 199a (low-T data), 266a, 273a	10.49	-4.14	2.77E-06
ethylcyclohexane	-368.5876	25363.63	48.84554	34 – 535	29	88a, 253a, 266a	9.48	-6.52	6.08E-07
Linear 1-Alkenes									
1-butene	-193.5447	13870.81	25.3347	77 – 291	10	28a, 124a, 136a	4.69	0.13	2.12E-04
1-hexene	-291.4130	20436.66	38.4871	68 – 430	16	199a, 254a, 272a	9.34	2.90	1.09E-05
1-octene	-286.3159	17849.77	37.9203	77 – 500	6	136a, 254a	7.12	0.35	4.08E-07
Normal Alkylbenzenes									
benzene	-195.5673	13544.694	25.8585	41 – 482	101	2a, 3a, 7a, 19a, 29a, 61a, 214a, 216a, 244a, 245a, 268a, 277a	4.08	-2.32	4.10E-04
toluene	-218.6392	15119.661	28.8653	33 – 527	39	3a, 19a, 29a, 244a, 246a	4.50	-0.72	1.19E-04

Table 9A2.2 – Continued

Compound	a_1	a_2	a_3	T Range/ °F	Data Sources # Points	Data Sources References	% AAD	% Bias	xhc @ 77 °F
ethylbenzene	-241.8211	16694.626	31.8721	32 – 400	54	5a, 29a, 88a, 108a, 111a, 136a, 147a, 169a, 187a, 188a, 210a, 247a, 274a	5.30	0.29	3.09E-05
propylbenzene	-330.4825	22994.478	43.8994	33 – 131	15	251a, 274a	8.41	6.46	8.20E-06
butylbenzene	-371.7299	24899.196	49.6592	33 – 212	26	247a, 251a, 274a	4.91	0.18	1.84E-06
pentylbenzene	-420.7929	29294.352	55.9266	45 – 113	11	274a	4.96	-0.49	4.18E-07
hexylbenzene	-465.8706	32444.280	61.9402	41 – 113	32	268a, 274a	4.85	-1.73	1.02E-07
Other Alkylbenzenes									
1,2-dimethylbenzene (o-xylene)	(deviation from ethylbenzene)			59 – 113	5	199a	7.47	7.47	3.26E-05
1,3-dimethylbenzene (m-xylene)	-215.0353	13932.150	28.4318	32 – 519	35	3a, 33a, 174a, 199a (low T)	12.22	2.48	3.14E-05
1,4-dimethylbenzene (p-xylene)	-206.4177	13330.984	27.2372	50 – 562	45	174a, 199a (low T), 247a, 259a	10.29	0.68	3.10E-05
isopropylbenzene	-262.5274	17838.856	34.67748	77 – 176	12	71a	0.08	-0.01	1.21E-05
1,3,5-trimethylbenzene	-248.0811	16349.596	32.77122	86 – 212	8	247a	3.10	0.07	8.84E-06
1,3-diethylbenzene	-311.3553	21748.495	41.11214	100 – 530	6	254a	3.32	0.09	4.02E-06
p-diisopropylbenzene	-308.4157	20014.725	40.74593	100 – 530	6	254a	5.89	0.22	3.01E-07

Table 9A2.2 – Continued

Compound	a_1	a_2	a_3	T Range/ °F	Data Sources # Points	Data Sources References	% AAD	% Bias	xhc @ 77 °F
Ethenylbenzene	-288.0113	19278.918	38.54914	45 – 149	11	5a, 119a	4.40	1.77	5.590E-05
Multiring Hydrocarbons									
1-methylnaphthalene	-220.5168	12603.309	29.35657	47 – 531	21	199a, 254a	6.17	0.28	3.670E-06
1-ethylnaphthalene	-247.3787	15072.320	32.71111	47 – 530	20	199a, 254a	4.55	0.15	1.132E-06

Notes

[a] If data only up to 284 °F are used, the AAD is reduced to 6.91%.

[b] Estimated the values of a(2) and a(3) by extrapolating the values for pentane to octane, and then determined the value of a(1) by fitting the solubility data of Joensson et al. [98a] at 59 and 68 °F.

[c] The lowest value at 34 °F from [250a] is below the melting point of cyclohexane, 43.8 °F.

[d] If data only up to 304 °F are used, the AAD is reduced to 7.90%.

Procedure 9A2.3 – Solubility of Solid, Polynuclear Aromatics in Water

Discussion

This procedure was last updated in 2005. The following equation is to be used to calculate the solubility of solid polynuclear aromatic hydrocarbons in water.

$$ln(x_{hc}) = a_1 + a_2/T + a_3\, ln(T) \qquad (9A2.3\text{-}1)$$

Where:

x_{hc}	=	*mole fraction of solid polynuclear aromatic hydrocarbon in water*
a_1, a_2, a_3	=	*component-specific parameters (see Table 9A2.4)*
T	=	*absolute temperature, in °R*

Table 9A2.4 also includes the temperature range (in °F) of the data for each hydrocarbon used in the regression with Eq. (9A2.3-1); the number of data points and their sources; the percent AAD (average absolute deviation) and bias (a positive bias indicates that the calculated values are, on average, higher than the experimental); and the solubility at 77 °F. If the temperature range of the data is too narrow (less than 50 °F), only parameters a_1 and a_2 are given in Table 9A2.4.

Procedure

Step 1: *Read the parameters a_1, a_2, and a_3 for the given hydrocarbon from Table 9A2.4.*

Step 2: *Calculate the solubility with Equation (9A2.3-1).*

Comments on Procedure 9A2.3

Purpose

This procedure calculates the solubility of solid polynuclear aromatic hydrocarbons in water over the temperature range given for each hydrocarbon in Table 9A2.4.

Limitations

Equation (9A2.3-1) is applicable at temperatures below the melting point of the hydrocarbon. The data have been obtained at near-atmospheric pressure but the effect of pressure on the solubility of the hydrocarbon in water is very small.

The valid temperature range for each hydrocarbon is given in Table 9A2.4. If all three parameters are given in Table 9A2.4, then extrapolation up to approximately 200 °F (if that temperature is below the melting point of the hydrocarbon) is generally permissible. However, when the temperature range of the data is less than 50 °F, only parameters a_1 and a_2 are given in Table 9A2.4. It is recommended that extrapolation be limited between 32 °F and 100 °F.

Reliability

As shown in Table 9A2.4, the average absolute deviation is less than 10 percent, except for anthracene, where the AAD is 15 percent. However, when all data are considered, the variation can be very wide. For example, the data for the solubility of anthracene in water at 77 °F cover the range 4.14×10^{-9} to 8.07×10^{-9}.

Literature Sources

The parameters listed in Table 9A2.4 were regressed from the data in the references given in the table. Solubility data only at 77 - 81 °F are reported in (199a) for several more polynuclear aromatic hydrocarbons. See also Table 9-0.2.

Example

Calculate the solubility of fluorene in water at 122 °F.

From Table 9A2.4, the appropriate parameters are a_1 is –380.76757, a_2 is 20361.30 and a_3 is 52.08392. The temperature is 122 + 459.67 = 581.67 °R. Substituting into Equation (9A2.3-1), the calculated x_{hc} value is 6.80×10^{-7}.

The only experimental value for the solubility of fluorene in water at 122 °F is 6.82×10^{-7} (222a, as reported in 199a, with a misprint in the mole fraction column, x_1. The correction changes the multiplier for x_1 from 10^7 to 10^8).

Table 9A2.4 – Parameters for Equation (9A2.3-1): Solubilities of Solid, Polynuclear Aromatic Hydrocarbons in Water

Compound	a_1	a_2	a_3	T Range/ °F	Data Sources		% AAD	% Bias	xhc @ 77 °F
					# Points	References			
naphthalene	-373.24613	21618.93	51.01156	32 – 167	63	199a, 268a	6.66	1.18	4.39E-06
acenaphthalene[a]	-334.02054	17740.54	45.56672	32 – 167	20	199a	6.32	0.86	4.75E-07
biphenyl	-332.69432	17633.99	45.48078	32 – 148	35	199a	4.11	0.80	8.55E-07
fluorene	-380.76757	20361.30	52.08392	32 – 167	27	199a, 268a	3.67	0.12	1.93E-07
anthracene[a]	-420.02594	21096.86	57.53568	32 – 167	45	199a, 268a	14.83	1.72	5.16E-09
phenanthrene	-350.23574	17490.54	47.98720	32 – 167	43	199a, 268a	5.40	0.25	1.10E-07
2-methylanthracene[a]	-1.3632759	-9957.797		43 – 88	10	199a	9.74	1.30	2.24E-09
1-methylphenanthrene	-1.551869	-8546.552		44 – 86	8	119a	2.04	0.03	2.57E-08
fluoranthene	-0.8449136	-9069.5788		47 – 86	10	199a, 268a	7.05	0.39	1.97E-08
pyrene[a]	-380.93125	19440.39	51.93974	32 – 167	38	199a, 268a	5.74	0.43	1.19e-08
benz[a]anthracene[a]	-2.55072	-9910.57		44 – 86	16	199a, 268a	6.21	0.59	7.45E-10
chrysene[a]	-7.53314	-8120.29		44 – 86	8	199a, 268a	4.13	0.92	1.44E-10
benzo[e]pyrene	-11.82626	-5275.62		47 – 89	10	199a	3.41	0.08	3.93E-10

[a] Additional data have been reported for the solubility in water of acenaphthene (257a), anthracene (252a, 257a, 270a), 2- and 9-methylanthracenes (252a), pyrene (270a), 9,10-dimethylanthracene (252a), benz[a]anthtacene [257a], chrysene [270a].

Table 9A2.5 – Solubilities of Selected Hydrocarbons and Nonhydrocarbons in Water at 77 °F Under Ambient Conditions

(See also Tables 9A2.2 and 9A2.4 for updated values)

Compound	Suggested Value (mole fraction)	Equilibrium[a] Condition	References
Hydrocarbons			
methane	2.60E-05	2	136a
ethane	3.35E-05	2	136a, 224a
propane	2.63E-05	2	136a, 224a
n-butane	2.15E-05	2	147a, 224a
isobutane	1.58E-05	2	136a,180a
n-pentane	9.87E-06	3	136a,171a,202a
isopentane	1.20E-05	3	88a
neopentane	1.08E-05	2	227a
n-hexane	1.98E-06	3	30a,136a,167a, 171a, 202a, 206a, 207a, 208a
2,2,4-trimethylpentane	3.86E-07	3	136a
cyclpropane	4.00E-04	2	93a
propylene	8.58E-05	2	125a
1-butene	7.15E-05	2	136a
1-pentene	3.81E-05	2	136a
trans-2-pentene	5.23E-05	3	136a
3-methyl-1-butene	8.47E-05	2	136a
1,3-butadiene	2.53E-04	2	144a
1,3-pentadiene[b]	1.70E-04	1	136a
acetylene	7.48E-04	2	91a
propyne	1.64E-03	2	94a
vinyl acetylene	6.85E-04	2	227a
benzene	4.16E-04	3	61a, 80a,136a, 207a
toluene	1.04E-043	3	80a,199a
ethylbenzene	2.84E-05	3	5a, 82a,108a, 136a, 199a, 210a
o-xylene	2.94E-05	3	136a,189a
m-xylene	2.77E-05	3	4a, 210a
p-xylene	3.05E-05	3	4a, 210a
xylenes-mixture[c]	2.92E-05	3	
isopropylbenzene	8.64E-06	3	209a
styrene	5.39E-05	3	119a
biphenyl	7.05E-07	3	222a
naphthalene	4.30E-06	4	194a

Table 9A2.5 (Continued)

Compound	Suggested Value (mole fraction)	Equilibrium[a] Condition	References
Organics			
methanol	infinitely soluble		234a
ethanol	infinitely soluble		234a
isobutanol	1.95E-02	1	196a
n-hexanol[g]	1.00E-04	1	196a
phenol	1.74E-02	1	196a, 202a
2-methyl-2-hexanol	1.51E-03	1	196a
3-methyl-3-hexanol	1.85E-03	1	196a
o-cresol	4.08E-03	1	196a
m-cresol	3.63E-03	1	196a
p-cresol	3.23E-03	1	196a
2,3-dimethyl-2-pentanol	2.39E-03	1	196a
2,4-dimethyl-2-pentanol	2.08E-03	1	196a
2,2-dimethyl-3-pentanol	1.27E-03	1	196a
2,3-dimethyl-3-pentanol	2.55E-03	1	196a
2,4-dimethyl-3-pentanol	1.09E-03	1	196a
3-ethyl-3-pentanol	2.61E-03	1	196a
2,2,3-trimethyl-3-pentanol	9.55E-04	1	196a
ethylene glycol	infinitely soluble		234a
acrolein[g]	6.83E-02	1	196a
diethyl ether	1.47E-02	1	196a
methyl n-butyl ether	1.82E-03	1	196a
methyl sec-butyl ether	3.27E-03	1	196a
methyl tert-butyl ether	8.10E-03	1	196a, 202a, 237a
ethyl n-propyl ether	3.83E-03	1	196a
ethyl isopropyl ether	4.91E-03	1	196a
di-n-propyl ether	8.65E-04	1	196a
methyl isobutyl ether	2.25E-03	1	196a
methyl isopropyl ether	1.58E-02	1	196a
methyl n-propyl ether	7.42E-03	1	196a
n-propyl isopropyl ether	4.41E-04	1	196a
carbonyl sulfide	3.90E-04	2	68a, 227a, 234a
methyl mercaptan	4.90E-03	2	68a
ethyl mercaptan	3.00E-03	1	68a
carbon disulfide	4.45E-04	2	234a
acetamide[g]	4.42E-01	1	196a
aniline	7.30E-03	1	202a
quinoline	8.90E-04	1	122a
n,n-dimethylformamide	infinitely soluble		84a
dinitrotoluene	2.67E-05	1	196a
nitrobenzene[g]	2.89E-04	1	196a
phenylenediamine	6.17E-03	1	196a
triethylamine	1.34E-02	1	196a, 202a
dichloromethane	4.17E-03	1	202a
dichloromethane[g]	4.30E-03	1	196a

Table 9A2.5 (Continued)

Compound	Suggested Value (mole fraction)	Equilibrium[a] Condition	References
1,1,2-trichloroethane[e]	6.01E-04	1	196a
tetrachloroethane	3.16E-04	1	196a
1,4-dichlorobenzene	9.82E-06	1	196a
epichlorhydrin[f]	1.29E-02	1	196a
ethyl chloride[d]	1.61E-03	1	196a
ethylene dichloride	1.61E-03	1	196a
1,1-dichloroethane	9.39E-04	1	196a
methyl chloroform[e]	1.82E-04	1	196a
1,2-dichloropropane	4.45E-04	1	196a
carbon tetrachloride	9.24E-05	1	196a
methyl ethyl ketone	7.72E-02	1	202a
methyl isobutyl ketone	3.30E-03	1	202a
methyl iodide	1.73E-03	1	196a
ethylene dibromide[g]	4.00E-04	1	196a
hydroquinone[g]	1.26E-02	1	196a
propylene oxide	8.02E-02	1	234a
phthalic anhydride	7.53E-04	1	196a
quinone	2.28E-03	1	196a
o-toluidine[e]	2.74E-03	1	196a
Inorganics			
ammonia	1.88E-01	2	92a, 227a
chlorine	1.63E-03	2	225a, 227a
hydrogen	1.35E-05	2	23a, 43a, 227a
hydrogen chloride	3.42E-01	2	92a
hydrogen sulfide	1.76E-03	2	33d, 227a
nitric oxide	3.48E-05	2	227a
phosphine	1.48E-04	1	227a
sulfur dioxide	2.46E-02	2	19d, 227a
sulfuric acid	infinitely soluble		
titanium tetrachloride	reacts with water		84a
arsine	1.61E-04	2	227a

a1 = Water-rich liquid-hydrocarbon-rich liquid equilibrium region
2 = Water-rich liquid-vapor equilibrium region
3 = Water-rich liquid-hydrocarbon-rich liquid-vapor equilibrium region
4 = Water-rich liquid-hydrocarbon solid equilibrium region
b =Value from 1,4-pentadiene.
c =Value averaged from the other xylene values
d =Value taken at a temperature of 64.4 °F
e =Value taken at a temperature of 68 °F
f =Value taken at a temperature of 86.1 °F
g =Value interpolated to a temperature of 77 °F from temperatures of 68 °F and 86 °F

Comments on Table 9A2.5

Purpose

This procedure was last updated in 1999. Table 9A2.5 presents recommended values for the solubility of various compounds in water at 77 °F and ambient pressure. The equilibrium condition for each value at specified conditions is also presented.

Reliability

All solubility values are based on one or more experimental values and are as reliable as the literature sources from which they were taken.

Literature Sources

The literature sources that the Technical Data Project Staff used to obtain the suggested values are presented in Table 9A2.5.

Procedure 9A2.6 – Solubility of Hydrocarbons in Water under Vapor-Liquid-Liquid Equilibrium Conditions at 77 °F

Discussion

This procedure was last updated in 1999. The following equation is to be used to predict the solubility of pure hydrocarbons in water under vapor-liquid- liquid equilibrium conditions at 77 °F:

$$-\log X_{hc} = a_1 + a_2 C_n + a_3 {C_n}^2 \qquad (9A2.6\text{-}1)$$

Where:

X_{hc}	=	*Solubility of hydrocarbon, mole fraction*
a_1, a_2, a_3	=	*Coefficients that depend on the homologous series of the given hydrocarbon (see Table 9A2.7)*
C_n	=	*Carbon number of the hydrocarbon*

Procedure

Step 1: *Determine the homologous series of the hydrocarbon and read the coefficients, a_1, a_2, and a_3 for this series from Table 9A2.7.*

Step 2: *Determine the carbon number of the hydrocarbon, Calculate the solubility using equation (9A2.6-1).*

Comments on Procedure 9A2.6

Purpose and Discussion

Procedure 9A2.6 is to be used for predicting solubilities of pure liquid hydrocarbons in water under vapor-liquid-liquid equilibrium conditions at 77 °F.

Limitations

Procedure 9A2.6 is applicable only to pure liquid hydrocarbons. It is not expected to be accurate for hydrocarbon mixtures. Also, the procedure is not applicable to hydrocarbons that cannot be classified as belonging to any one of the 9 homologous series listed in Table 9A2.7.

Reliability

This procedure reproduces the experimental data with an average error of 10 percent.

Literature Sources

The original Procedure 9A2.6 was developed by V. N. Kabadi and R. P. Danner, *Hydrocarbon Processing* **58** [5] 245 (1979). It was modified by the API Technical Data Book Project Staff (1996).

Example

Find the solubility of benzene in water at 77 °F under vapor-liquid-liquid equilibrium conditions.

From Table 9A2.7 for benzene, $a_1 = -0.4628$, $a_2 = 0.6916$ and $a_3 = -0.8410\times10^{-2}$. The carbon number of benzene is 6. Using equation (9A2.6-1) the solubility is calculated by to be 4.13×10^{-4}.

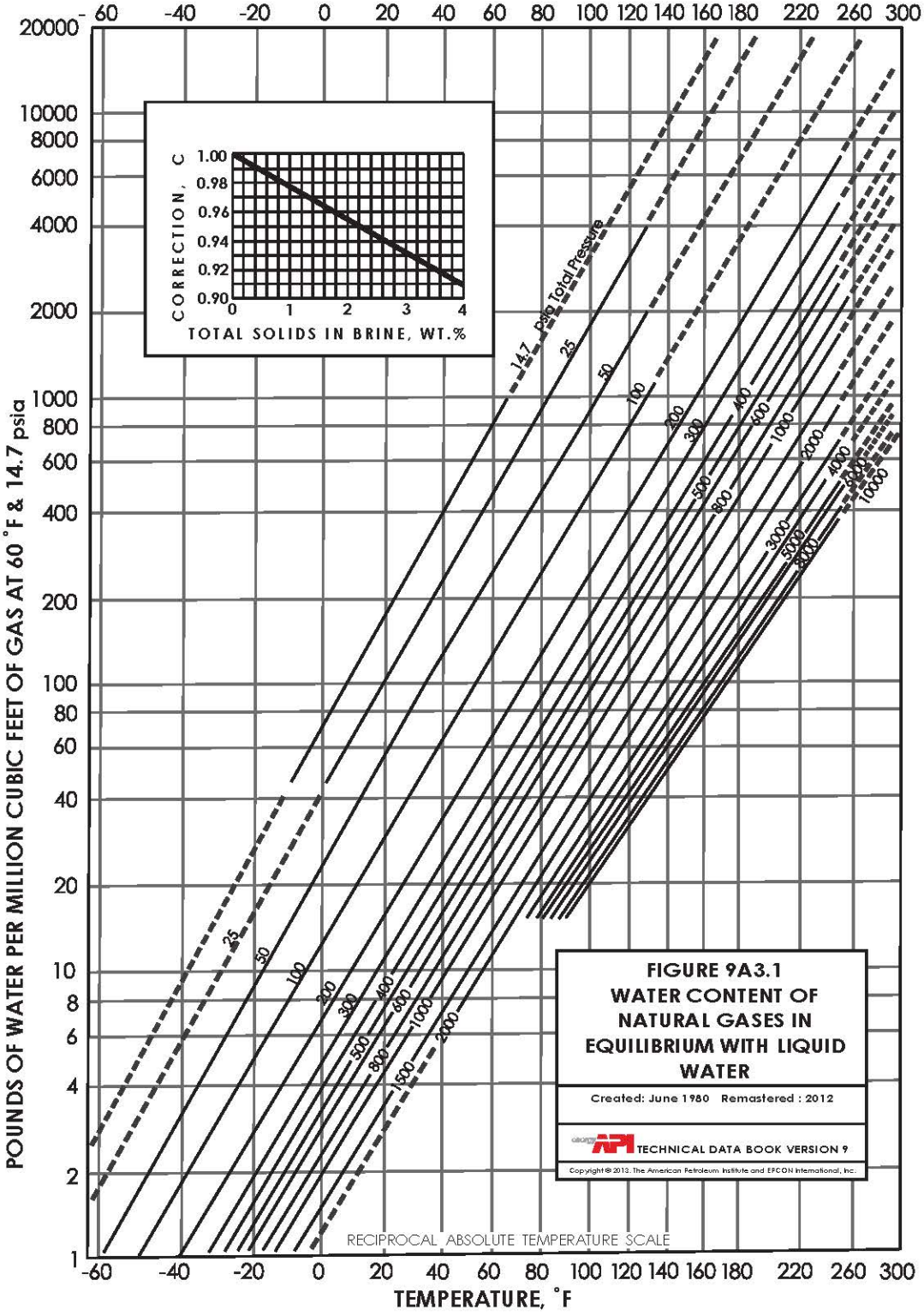
The experimental solubility of benzene in water at 77 °F is 4.11×10^{-4} (146a).

Table 9A2.7 – Coefficients for Procedure 9A2.6

	Coefficients for Equation (9A2.6 1)		
Homologous Series	**a_1**	**a_2**	**a_3**
n-paraffin	1.6708	0.6386	0.005538
paraffin with one branch	9.6776	–2.2691	0.263567
paraffin with two branches	0.0000	1.0157	–0.020577
naphthene	4.4465	–0.3285	0.063729
naphthene with one branch	11.8697	–2.5294	0.232027
alkene	8.4469	–1.6631	0.172448
cycloalkene	0.4247	0.5682	0.012414
acetylene	–0.9415	0.9839	–0.007961
benzene or *n*-alkylbenzene	–0.4628	0.6916	–0.008410

9A3 Water Content of Hydrocarbon Gases

Figure 9A3.1 – Water Content of Natural Gases in Equilibrium with Liquid Water



Comments on Figure 9A3.1

Purpose

This procedure was last updated in 1999. This figure shows the water content of natural gas in equilibrium with water. A salinity correction chart is provided for use when the liquid-water phase contains salt.

A calculation method has been developed and is presented in the special comments section.

Limitations

Figure 9A3.1 is reliable for natural gases of specific gravity of 0.8 or less (air = 1.0). A molecular weight correction chart is available in the literature (141a). This correction chart is not given here, however, because in a study with a few defined hydrocarbon gas systems, absolute errors as high as 110 percent were found and there was no significant trend to the errors as a function of specific gravity.

Reliability

For natural gases with a specific gravity of 0.8 or less, the standard deviation of the chart from published data is 4 percent, with a negligibly small bias.

Notation

The broken lines indicate extrapolations beyond the limits of the available literature data.

Special Comments

To use the salinity correction, the water content read from the main chart is multiplied by the correction factor C, which corresponds to the appropriate salt concentration in the liquid water phase.

At low temperature and high pressures, hydrate formation can occur (see Section 9B).

The following equation is to be used to calculate the pounds of water per million cubic feet of natural gas at 60 °F and 14.7 psia.

$$Y = (-0.0227Wt + 1)10^{\left[-2.3205[log\,P]^{0.53} - \frac{3888}{T} + 12.9\right]} \qquad (9A3.1\text{-}1)$$

Where:

Y	=	*Pounds of water per million cubic feet of natural gas at 60 °F and 14.7 psia*
T	=	*Absolute temperature °R*
P	=	*Pressure psia*
Wt	=	*wt% of total solids in brine*

This equation has an estimated reliability of 9.5% with a –0.9% bias for natural gases with a specific gravity of 0.8 or lower and is only reliable for natural gases with a specific gravity of 0.8 or less (air =1.0).

Literature Source

Figure 9A3.1 was adapted from McKetta and Wehe, *Petrol Refiner* **37** [8] 153 (1958).

Example

Find the water content of a natural gas at 100 °F and 300 pounds per square inch absolute that is in equilibrium with liquid-water phase containing 0.4 percent salt.

For pure water, the water content is given by the main chart in Figure 9A3.1 at 160 pounds water per million cubic feet of gas. From the salinity correction chart, the correction factor C is 0.99. Therefore, the corrected water content is (0.99)(160) = 158 pounds of water per million cubic feet of gas.

The equation presented in the special comments gives a water content of 157.1 pounds of water per million cubic feet of gas.

9A5 Salt Effect on Solubility of Hydrocarbons in Water

Procedure 9A5.1 – Solubility of Hydrocarbons in Aqueous Salt Solutions

Discussion

This procedure was last updated in 1999. Knowing the solubility of a hydrocarbon in water, the following equation is to be used to calculate the solubility of the hydrocarbon in an aqueous salt solution:

$$log\frac{X}{X_0} = -K_S C_S \qquad (9A5.1\text{-}1)$$

Where:

X	=	*Solubility of hydrocarbon in salt solution, mole fraction*
X_0	=	*Solubility of hydrocarbon in water, mole fraction*
K_S	=	*Setschenow constant, in liters per gram equivalent (Constants for hydrocarbons in different salt solutions at different temperatures and pressures are listed in Table 9A5.2.)*
C_S	=	*Salt concentration of solution, in gram equivalents per liter*

Procedure

Step 1: *Knowing the temperature and pressure, read values of K_S and X_0 for the hydrocarbon-salt-water system from Table 9A5.2. If K_S and X_0 are not given for the system of interest, the procedure cannot be used. If K_S and X_0 are listed at temperatures and pressures close to the temperature and pressure of interest, calculate values of K_S and X_0 by interpolation or extrapolation. If the temperature and pressure of interest are far from those given, the procedure is not applicable.*

Step 2: *Calculate the solubility of the hydrocarbon in the aqueous salt solution using equation (9A5.1-1).*

Comments on Procedure 9A5.1

Purpose

Procedure 9A5.1 is presented as a method for calculating the solubility of hydrocarbons in aqueous salt solutions, knowing the solubility in pure liquid water.

Limitations

Procedure 9A5.1 can be used only for the hydrocarbon-saltwater systems listed in Table 9A5.2. Also, it can be used only in the range of temperatures and pressures listed in Table 9A5.2. (Interpolations within, or moderate extrapolations out of, the given temperature-pressure range are permissible.) The procedure is not recommended at temperatures and pressures far from the values listed in Table 9A5.2.

Reliability

Equation (9A5.1-1), with K_S and X_0 at different temperatures and pressures listed in Table 9A5.2, reproduces the experimental data to within an average error of ± 10 percent.

Literature Sources

Equation (9A5.1-1) was taken from the original work of J. Setschenow, Z. *Phys. Chem*. **4** 117 (1889). A discussion of the relationship is also given by Long and McDevit, *Chem. Rev.* **51** 128 (1952).

Example

Find the solubility of methane in a 4 g/L aqueous sodium chloride solution at a temperature of 125 °F and 500 atmospheres.

From Table 9A5.2, for the methane-NaCl-water system at 124.7 °F and 500 atmospheres, X_0 = 0.00373 mole fraction and K_S = 0.120. Assume the same values at 125 °F and 500 atmospheres.

Then, from equation (9A5.1-1):

$$-\log\frac{X}{X_0} = 0.120(4)$$

$$\log\frac{X}{X_0} = -0.48$$

$$\frac{X}{X_0} = 0.3311$$

$$X = 0.3311(0.00373)$$

$$X = 0.00124$$

The experimental value for solubility is 0.0013 (160a).

Table 9A5.2 – Literature Sources and Setschenow Constants (for Procedure 9A5.1) for Solubility of Hydrocarbons in Different Aqueous Salt Solutions

Solute	Salt	Temperature (°F)	Pressure (psia)	$X_0 \times 10^3$ (mole fraction)	K_s (L/g equivalent)	Reference
methane	NaCl	32.0	14.7	0.0449	0.194	57a, 232a
		50.0	14.7	0.0344	0.170	232a
		54.6	14.7	0.0307	0.153	147a
		86.0	14.7	0.0183	0.127	147a, 232a
		121.0	14.7	0.0175	0.111	147a
		161.0	14.7	0.0155	0.102	147a
		86.0	300	0.457	0.114	53a
		86.0	400	0.599	0.113	53a
		86.0	500	0.738	0.10	53a
		86.0	600	0.864	0.096	53a
		124.7	1470	1.430	0.122	160a
		124.7	2940	2.280	0.119	160a
		124.7	4410	2.870	0.122	160a
		124.7	5880	3.340	0.121	160a
		124.7	7350	3.730	0.120	160a
		124.7	8820	4.090	0.119	160a
		216.5	2940	2.210	0.109	160a
		216.5	4410	2.870	0.108	160a
		216.5	5880	3.330	0.112	160a
		216.5	7350	3.850	0.120	160a
		216.5	8820	4.190	0.112	160a
		257.0	1470	1.430	0.132	160a
		257.0	2940	2.320	0.117	160a
		257.0	4410	2.960	0.121	160a
		257.0	5880	3.430	0.119	160a
		257.0	7350	3.960	0.124	160a
		257.0	8820	4.300	0.121	160a
methane	$CaCl_2$	77.0	300	0.501	0.132	53a
		77.0	400	0.650	0.109	53a
		77.0	500	0.802	0.105	53a
		77.0	600	0.939	0.103	53a
		86.0	400	0.599	0.091	53a
		86.0	500	0.734	0.084	53a
		86.0	500	0.734	0.084	53a
methane	LiCl	54.6	14.7	0.037	0.130	147a
		85.8	14.7	0.183	0.097	147a
		121.0	14.7	0.0175	0.082	147a
		161.0	14.7	0.0155	0.077	147a
methane	KI	54.6	14.7	0.0307	0.130	147a
		85.8	14.7	0.0183	0.097	147a

Table 9A5.2 (Continued)

Solute	Salt	Temperature (°F)	Pressure (psia)	$X_0 \times 10^3$ (mole fraction)	K_s (L/g equivalent)	Reference
		121.0	14.7	0.0175	0.071	147a
		161.0	14.7	0.0155	0.054	147a
ethane	NaCl	32.0	14.7	0.0161	0.198	44a
		54.6	14.7	0.0411	0.184	147a
		68.0	14.7	0.0403	0.175	44a
		85.8	14.7	0.0272	0.162	147a
		121.0	14.7	0.0202	0.145	147a
		161.0	14.7	0.0166	0.135	147a
propane	NaCl	54.6	14.7	0.0396	0.216	147a
		85.8	14.7	0.0234	0.194	147a
		121.0	14.7	0.0157	0.178	147a
		161.0	14.7	0.0123	0.165	147a
propane	LiCl	54.6	14.7	0.0396	0.175	147a
		85.8	14.7	0.0234	0.152	147a
		121.0	14.7	0.0157	0.138	147a
		161.0	14.7	0.0123	0.138	147a
propane	KI	54.6	14.7	0.0396	0.121	147a
		85.8	14.7	0.0234	0.102	147a
		121.0	14.7	0.0157	0.085	147a
		161.0	14.7	0.0123	0.067	147a
n-butane	NaCl	32.0	14.7[a]	0.059	0.283	182a
		50.0	14.7[a]	0.0407	0.301	182a
		54.6	14.7	0.0342	0.243	147a
		68.0	14.7[a]	0.0259	0.250	182a
		85.8	14.7	0.0192	0.217	147a
		121.0	14.7	0.0114	0.194	147a
		161.0	14.7	0.0083	0.150	147a
n-butane	KI	54.6	14.7	0.0342	0.109	147a
		85.8	14.7	0.0192	0.098	147a
		121.0	14.7	0.0114	0.080	147a
		161.0	14.7	0.0083	0.059	147a
n-butane	KCl	54.6	14.7	0.0342	0.200	147a
		85.8	14.7	0.0192	0.182	147a
		121.0	14.7	0.0114	0.164	147a
		161.0	14.7	0.0083	0.144	147a
n-butane	HCl	54.6	14.7	0.0342	0.080	147a
		85.8	14.7	0.0192	0.049	147a
		121.0	14.7	0.0114	0.031	147a
		161.0	14.7	0.0083	0.028	147a
n-butane	$BaCl_2$	54.6	14.7	0.0347	0.250	147a

Table 9A5.2 (Continued)

Solute	Salt	Temperature (°F)	Pressure (psia)	$X_0 \times 10^3$ (mole fraction)	K_s (L/g equivalent)	Reference
		85.8	14.7	0.0192	0.210	147a
		121.0	14.7	0.0114	0.180	147a
		161.0	14.7	0.0083	0.165	147a
n-butane	$LaCl_3$	54.6	14.7	0.0347	0.182	147a
		85.8	14.7	0.0192	0.154	147a
		121.0	14.7	0.0114	0.154	147a
		161.0	14.7	0.0083	0.140	147a
n-pentane	NaCl	77.0	[b]	0.00964	0.227	171a
ethene	NaCl	54.6	14.7	0.103	0.140	147a
		77.0	14.7[a]	0.080	0.140	159a
		85.8	14.7	0.0722	0.127	147a
		121.0	14.7	0.0540	0.114	147a
		161.0	14.7	0.0445	0.101	147a
	LiCl	54.6	14.7	0.103	0.104	147a
		85.8	14.7	0.0722	0.089	147a
		121.0	14.7	0.0540	0.082	147a
		161.0	14.7	0.0445	0.083	147a
	KI	54.6	14.7	0.103	0.070	147a
		85.8	14.7	0.0722	0.061	147a
		121.0	14.7	0.0540	0.050	147a
		161.0	14.7	0.0445	0.036	147a
	$LaCl_3$	54.6	14.7	0.1030	0.112	147a
		85.8	14.7	0.0722	0.100	147a
		121.0	14.7	0.540	0.105	147a
		161.0	14.7	0.0445	0.091	147a
	$BaCl_2$	77.0	14.7[a]	0.080	0.137	159a
	NH_4NO_3	77.0	14.7[a]	0.080	0.051	159a
	Na_2SO_4	77.0	14.7[a]	0.080	0.198	159a
	Na_2SO_3	77.0	14.7	0.080	0.172	159a
	KOH	59.0	14.7	0.1005	0.177	16a
	NaOH	59.0	14.7	0.1005	0.195	16a
	NH_4OH	59.0	14.7	0.1005	0.0156	16a
	Na_3SO_4	59.0	14.7	0.1005	0.225	16a
ethyne	$Ba(OH)_2$	59.0	14.7	1.020	–0.057	16a

Table 9A5.2 (Continued)

Solute	Salt	Temperature (°F)	Pressure (psia)	$X_0 \times 10^3$ (mole fraction)	K_s (L/g equivalent)	Reference
ethyne	NH_4OH	59	14.7	1.020	–0.0032	16a
	NaOH	59	14.7	1.020	0.165	16a
	KOH	59	14.7	1.020	0.137	16a
	Na_2SO_4	59	14.7	1.020	0.267	16a
	H_2SO_4	59	14.7	1.020	0.0650	16a
methylcyclopentane	NaCl	77	[b]	0.0402	0.225	171a
benzene	Na_2SO_4	77	[b]	0.410	0.274	139a
	$BaCl_2$	77	[b]	0.410	0.167	139a
	NaOH	77	[b]	0.410	0.256	139a
	NaF	86	[b]	0.426	0.254	191a
	NaCl	77	[b]	0.410	0.195	129a, 135a, 139a
	KCl	77	[b]	0.410	0.166	139a
	NaBr	77	[b]	0.410	0.155	139a
	LiCl	77	[b]	0.410	0.141	139a
	RbCl	77	[b]	0.410	0.140	139a
	KBr	77		0.410	0.119	139a
	$NaNO_3$	77	[b]	0.410	0.119	139a
	$NaClO_4$	77	[b]	0.410	0.106	139a
	NH_4Cl	77	[b]	0.410	0.095	139a
	NaI	77	[b]	0.410	0.095	139a
	CsCl	77	[b]	0.410	0.088	139a
	HCl	77	[b]	0.410	0.048	139a
	NH_4Br	77		0.426	0.041	191a
	CsI	77	[b]	0.410	–0.006	139a
	$KO_2C_7H_5$	86	[b]	0.426	–0.006	191a
	$HClO_3$	77	[b]	0.410	–0.041	139a
	$(CH_3)_4NBr$	86	[b]	0.426	–0.240	191a

Table 9A5.2 (Continued)

Solute	Salt	Temperature (°F)	Pressure (psia)	$X_0 \times 10^3$ (mole fraction)	K_s (L/g equivalent)	Reference
toluene	NaCl	77	[b]	0.101	0.205	171a
ethylbenzene	NaCl	77	[b]	0.0260	0.242	147a
naphthalene	Na_2SO_4	77	[b]	0.00420	0.356	162a
	NaCl	77	[b]	0.00420	0.260	55a, 135a, 162a
	KCl	77	[b]	0.00420	0.204	162a
	LiCl	77	[b]	0.00420	0.180	162a
	NaBr	77	[b]	0.00420	0.169	162a
	$NaCl0_4$	77	[b]	0.00520	0.101	162a
	HCl	77	[b]	0.00420	0.046	162a
	$HClO_4$	77	[b]	0.00420	–0.081	162a
	Na_2SO_4	32.18	[b]	0.0016	0.367	162a
	NaCl	32.18	[b]	0.0016	0.232	162a
	LiCl	32.18	[b]	0.0016	0.191	162a
	NaBr	32.18	[b]	0.0016	0.166	162a
	HCl	32.18	[b]	0.0016	0.055	162a
biphenyl	Na_2S0_4	77	[b]	0.00086	0.423	162a
	NaCl	77	[b]	0.00086	0.275	55a, 162a
	KCl	77	[b]	0.00086	0.253	162a
	LiCl	77	[b]	0.00086	0.218	162a
	NaBr	77	[b]	0.00086	0.209	162a
	$NaCl0_4$	77	[b]	0.00086	0.114	162a
biphenyl	HCl	77	[b]	0.00086	0.071	162a
	$HCl0_4$	77	[b]	0.00086	–0.116	162a
phenanthrene	NaCl	77	[b]	0.000108	–0.336	55a, 194a
fluorene	NaCl	77	[b]	0.000214	0.267	135a
anthracene	NaCl	77	[b]	0.76×10^{-5}	0.238	135a, 194a
2-methylanthracene	NaCl	77	[b]	0.37×10^{-5}	0.336	135a
l-methylphenanthrene	NaCl	77	[b]	0.25×10^{-4}	0.211	135a
pyrene	NaCl	77	[b]	0.12×10^{-4}	0.286	135a, 194a
fluoranthene	NaCl	77	[b]	0.23×10^{-4}	0.339	135a
chrysene	NaCl	77	[b]	0.16×10^{-4}	0.336	135a
1,2-benzanthracene	NaCl	77	[b]	0.11×10^{-3}	0.354	135a
1-methylnaphthalene	NaCl	77	[b]	0.0038	0.191	194a
1-ethylnaphthalene	NaCl	77	[b]	0.00115	0.269	194a
benz(e)pyrene	NaCl	77	[b]	0.34×10^{-6}	0.426	194a

a Partial pressure of gas. b System pressure.

9A6 Phase Equilibrium Calculations for Water-Hydrocarbons Systems

Procedure 9A6.1 – Modified Soave-Redlich-Kwong Equation of State for Phase Equilibrium Calculations for Water-Hydrocarbons Systems

Discussion

This procedure was last updated in 1999. The compositions of coexisting phases for the two-phase vapor-liquid and liquid-liquid and three-phase vapor-liquid-liquid equilibria for hydrocarbon-water systems are estimated using a modified Soave-Redlich-Kwong equation of state (101a, 201a). To compute these compositions for an *n*-component system with *m* phases in equilibrium, the equation of state needs be solved to satisfy the following relationships:

$$T^1 = T^2 = T^3 \ldots = T^m$$
$$P^1 = P^2 = P^3 \ldots = P^m$$
$$f_i^1 = f_i^2 = f_i^3 \ldots = f_i^m, \;\; i = 1,2 \ldots n$$

The first two relationships equate the temperature and pressure in each phase, and the next *n* equations equate the fugacities of the individual components in each phase.

A simplified flow chart of the equilibrium calculation is shown in the procedure diagram.

The feed composition and an estimate of the *K* values are used to initiate the calculation.

The calculation steps are as follows:

Step 1: *Make an equilibrium calculation using a set of assumed K values and the known feed composition. This gives a set of compositions of the coexisting phases.*

Step 2: *Use the compositions to compute the composition-dependent parameters in the equation of state. Based on the known temperature and pressure, find the molar volumes of the different phases.*

Step 3: *Compute the fugacities of all components in each phase from the equation of state.*

Step 4: *Check the fugacities. If the fugacities of all components are the same in each phase, stop the calculation.*

Step 5: *If the fugacities in each phase differ, readjust the K values and return to Step 1.*

Similar schemes apply for dew– and bubble–point calculations.

The following equations apply to the modified Soave procedure for water-hydrocarbon systems.

A. Phase Volumes

The equation of state for both the liquid and the vapor phase needs to be solved for the phase volumes based on the phase compositions, temperature, and pressure. The compressibility factors and the phase volumes in both the liquid and the vapor phases are given by equations (9A6.1-1) and (9A6.1-2).

$$Z = \frac{V}{(V-b)} - \frac{a}{RT(V+b)} \qquad (9A6.1\text{-}1)$$

Or

$$V^3 - \frac{RT}{P}V^2 - \left(b^2 + \frac{RT}{P}b - \frac{a}{P}\right)V - \frac{ab}{P} = 0 \qquad (9A6.1\text{-}2)$$

Where:

Z	=	*compressibility factor*
V	=	*molar volume in lb-mole/ft^3*
T	=	*absolute temperature in °R*
R	=	*gas constant*
	=	*10.731 psia ft^3/lb-mole °R*
a	=	*energy parameter*
b	=	*volume parameter*

The equation of state may be solved iteratively for *Z* or it may be rearranged to a cubic form in *V* and solved analytically. The latter is recommended because it minimizes the possibility of selecting the incorrect volume root. When the cubic equation is solved, the largest volume is the saturated vapor volume, and the smallest volume is the saturated liquid volume. The middle root has no physical significance as far as the calculation is concerned. In the equilibrium calculation, note that no matter which solution technique for the volume is employed, it needs to be repeated for all phases, since *a* and *b* depend on the composition of each phase.

B. Fugacity Coefficient

The fugacity of a component in a phase may be calculated once the fugacity coefficient has been evaluated.

The relationship between the fugacity and the fugacity coefficient is given by equation (9A6.1-3).

$$f_i^N = \phi_i^N x_i P \qquad (9A6.1\text{-}3)$$

Where:

f_i^N	=	*fugacity of Component i in Phase N*
ϕ_i^N	=	*fugacity coefficient of Component i in Phase N*
x_i	=	*mole fraction of Component i in Phase N*
P	=	*total pressure*

In terms of the modified Soave equation, the fugacity coefficient in a liquid or a vapor phase for water-hydrocarbon systems may be calculated from equation (9A6.1-4) once the volume of that phase has been determined:

$$ln\,\phi_i^N = \frac{b_i}{b}(Z-1) - ln(Z-B) - \frac{A}{B}\left[\frac{2\sum_j x_j a_{ij} + \varepsilon}{a} - \frac{b_i}{b}\right] ln\left(1+\frac{B}{Z}\right) \qquad (9A6.1\text{-}4)$$

Where:

b_i = *volume parameter of Component i*

a_{ij} = *energy parameter for an ij pair*

$$A = \frac{aP}{R^2T^2}$$

$$B = \frac{bP}{RT}$$

$$\varepsilon = \sum_j \left(2x_W x_j - x_w^2 x_j\right) a'_{wj}\,, if\ i\ refers\ to\ water$$

$$\varepsilon = x_w^2 a'_{wi} - \sum_j x_w^2 x_j a'_{wj}\,, if\ i\ refers\ to\ hydrocarbon$$

a'_{wj} = *secondary energy parameter for a water–hydrocarbon pair*

C. Equation Constants for Pure Components

The equation constants for all pure components are calculated from the critical temperature, the critical pressure and the acentric factor.

$$a_i = 0.42747\left(\frac{R^2T_{ci}^2}{P_{ci}}\right)\alpha_i \qquad (9A6.1\text{-}5)$$

$$b_i = 0.08664\left(\frac{RT_{ci}}{P_{ci}}\right) \qquad (9A6.1\text{-}6)$$

Where:

a_i	=	*energy parameter for Component i*
b_i	=	*volume parameter for Component i*
T_{ci}	=	*critical temperature of Component i, in °R*
P_{ci}	=	*critical pressure of Component I, in psia*
R	=	*gas constant*
	=	*10.731 psia ft³/lb-mole °R*

For hydrocarbons, α_i is given by

$$\alpha_i = \left[1 + S_i\left(1 - \sqrt{T_{r_i}}\ \right)\right]^2 \qquad (9A6.1\text{-}7)$$

Where:

T_{r_i} = *reduced temperature of i* = $\frac{T}{T_{c_i}}$

S_i = $0.48508 + 1.55171\omega_i - 0.15613\omega_i^2$

ω_i = *acentric factor of i*

For water, α_i is given by

$$\alpha_w = \left[1 + 0.662\left(1 - T_{r_w}^{0.8}\right)\right]^2 \qquad (9A6.1\text{-}8)$$

Where:

T_{r_w} = *reduced temperature of water* = T/T_{c_w}.

D. Equations for Composition-Averaged Parameters

The composition-averaged parameters *a* and *b* are calculated from equations (9A6.1-9) and (9A6.1-10):

$$a = \sum\sum x_i x_j a_{ij}\left(1 - k_{ij}\right) + \sum a'_{wi} x_w^2 x_i \qquad (9A6.1\text{-}9)$$

$$b = \sum x_i b_i \qquad (9A6.1\text{-}10)$$

Where:

a_{ij} = $\sqrt{a_i a_j}$

k_{ij} = *binary interaction coefficient.*

a'_{wi} = *secondary energy parameter for interaction between water and Hydrocarbon i.*

E. Binary Interaction Coefficient

The binary interaction coefficients for hydrocarbon-hydrocarbon pairs are zero. The binary interaction coefficients between water and different homologous series of hydrocarbons are given in Table 9A6.2.

F. Secondary Energy Parameter a'_{wi}

The secondary energy parameters for a water-hydrocarbon pair are given by a group contribution method. Different groups constituting hydrocarbons are defined. The secondary energy parameter is given by the sum of the group contributions of different groups forming a hydrocarbon molecule multiplied by a temperature dependence in terms of reduced

temperature of water: Equations (9A6.1-11) and (9A6.1-12) give the secondary energy parameter:

$$a'_{wi} = G_i\left[1 - T_{r_w}^{0.8}\right] \qquad (9A6.1\text{-}11)$$

$$G_i = \sum_j g_j \qquad (9A6.1\text{-}12)$$

Where:

G_i	=	*sum of the group contributions of different groups forming a hydrocarbon molecule, in atm $(m^3/mole)^2$*
T_{r_w}	=	*reduced temperature of water = T/T_{CW}*
g_j	=	*group contribution of group j*

Different hydrocarbon groups and their group contribution are given in table 9A6.3

Procedure

Step 1: *For water and hydrocarbons in the mixture, obtain the critical temperature and pressure and the acentric factor from the Pure Component Properties program.*

Step 2: *Obtain a_i and b_i from equations (9A6.1-5) through (9A6.1-8).*

Step 3: *Obtain a set of initial K values for the mixture based on ideal K values or some other suitable source.*

Step 4: *Based on the desired objective (equilibrium flash, dew or bubble point), perform a flash calculation to obtain T, P and the compositions of the coexisting phases based on the assumed K values.*

Step 5: *Using T and the phase compositions, apply equations (9A6.1-9) through (9A6.1-11) with the appropriate k_{ij} and G_i to obtain mixture parameters a and b in the different phases.*

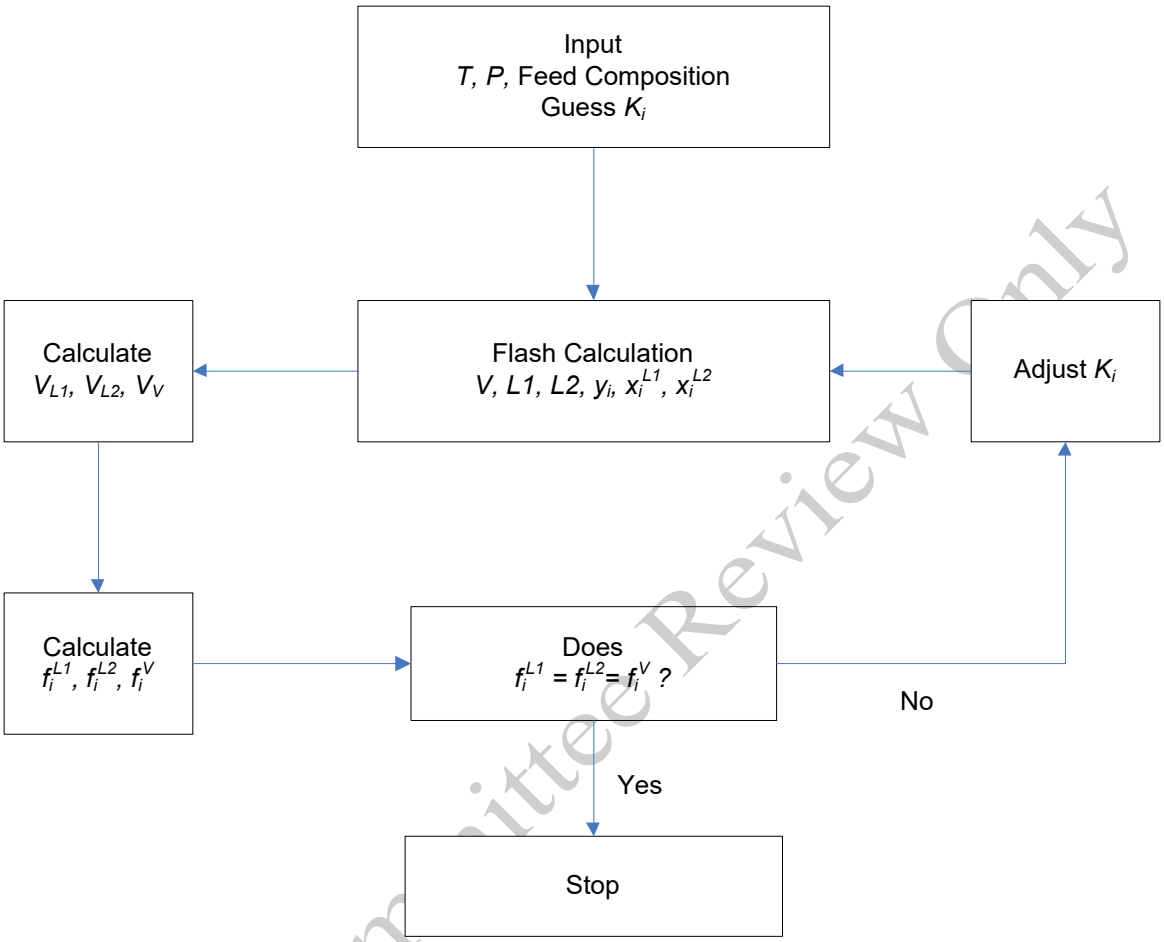
Step 6: *Find the liquid and vapor-phase volumes from equation (9A6.1-2) using the appropriate a and b parameters.*

Step 7: *Compute the fugacity coefficients of all components in all the phases from equation (9A6.1-4).*

Step 8: *Check the fugacities to see if they match in all the phases for each component.*

Step 9: *If they do not match, adjust the estimated K values and proceed to Step 4. If they do match, stop the calculation.*

Procedure Diagram for Phase Composition Calculations



Note: *The diagram is for a three-phase calculation. L1 and L2 correspond to the two liquid phases and V to the vapor phase. x_i^{L1} and x_i^{L2} correspond to compositions in the two liquid phases and y_i to the composition in the vapor phase. The same procedure would be followed for a two-phase calculation.*

Comments on Procedure 9A6.1

Purpose

This procedure is to be used to estimate the compositions of the coexisting phases for hydrocarbon-water systems under vapor-liquid, liquid-liquid or vapor-liquid-liquid equilibrium.

Limitations

The correlation was developed for hydrocarbons up to C_{10}. Caution is recommended when using when applying it to heavier hydrocarbons, close to the three-phase critical point, or at temperatures greater than 550 °F.

The correlation cannot be used if a hydrocarbon cannot be classified as belonging to one of the homologous series listed in Table 9A6.2.

Reliability

For hydrocarbons up to C_{10} and temperatures below 550 °F, an average error of 37 percent may be expected for solubility of water in hydrocarbons and 45 percent for solubility of hydrocarbons in water. The corresponding errors in the *K* values of water and hydrocarbons may be expected to be about 30 percent.

Literature Sources

The original Soave equation of state is from G. Soave, *Chem, Eng. Sci*. **27** 1197 (1972). It was modified for water-hydrocarbon systems by V. N. Kabadi and R. P. Danner (101a).

Table 9A6.2 – Binary Interaction Coefficients for Procedure 9A6.1

Homologous Series	k_{wi}
alkanes	0.500
alkenes	0.393
dialkenes	0.311
alkynes	0.348
naphthenes	0.455
cycloalkenes	0.355
aromatics	0.315

Table 9A6.3 – Group Contribution Parameters for Procedure 9A6.1

Group j	g_j x 10^5 [atm$(m^3/\text{mole})^2$]
CH_4	1.3580
--- CH_3	0.9822
--CH_2---	1.0780
— CH	0.9728
— C —	0.8687
—CH_2 — (Cyclic)	0.7488
— CH (cyclic)	0.7352
— CH = CH —(cyclic)[a]	0.6180
$CH_2=CH_2$	1.7940
$CH_2=CH$–	1.3450
$CH_2=C$–	0.9066
HC ≡ CH	1.6870
HC ≡ C –	1.1811
–CH = (aromatic)	0.5117
– C = (aromatic)	0.3902

[a] This value is obtained from very few data; therefore, it might not be reliable.

9A7 Solubility of Nonhydrocarbon Gases in Water

Procedure 9A7.1 – Henry's Constants for Selected Gases in Water

Discussion

This procedure was last updated in 2011. The following equation, which originally was intended only for gases dissolved in water, uses four parameters to represent the temperature dependence of the Henry's constants for a variety of organic and inorganic components. The parameters in this equation have been rearranged so that the first three terms are the same as those used for the solubility of liquid hydrocarbons in water (see Procedure 9A2.1):

$$\ln H = b_1 + b_2/T + b_3 \ln T + b_4 T \qquad (9A7.1\text{-}1)$$

Where:

H = *the Henry's constant, in (psia) per unit mole fraction of the solute;*

T = *the absolute temperature, in °R*

b_1, b_2, b_3, b_4 = *the parameters given in Table 9A7.2*

The addition of the b_4T term can be useful when relatively smooth *H* values are available over a wide temperature range. Otherwise, the addition of the b_4T can lead to qualitatively poor extrapolations.

Table 9A7.2 includes the temperature range (in °F) of the data used in the regression with Equation (9A7.1-1); the number of data points and their sources; the percent AAD (average absolute deviation) and bias (a positive bias indicates that the calculated values are, on average, higher than the experimental); and the solubility at 77 °F calculated with Equation (9A7.1-1) and the parameters. Footnotes are provided when any of this information is not available.

Procedure

Step 1: *Obtain the parameters b_1, b_2, b_3, b_4 from Table 9A7.2.*

Step 2: *Calculate the Henry's constant of the gas or liquid with Equation (9A7.1-1) at the desired temperature.*

Comments on Procedure 9A7.1

Purpose

This procedure calculates the Henry's constants of gases and liquids dissolved in water over the temperature range given for each component in Table 9A7.2.

Limitations

The valid temperature range for each component is given in Table 9A7.2. Limited extrapolation is generally permissible.

Henry's constants can be calculated for gases from solubility data at $p < p_3$, the three-phase equilibrium pressure (or at $T > T_{3c}$, the three-phase critical temperature) or for liquids from solubility data at $p \geq p_3$. For hydrocarbon and other gases that are slightly soluble in water (say, $x_i < 0.03$) and the total pressure is less than 1000 psia the key vapor-liquid equilibrium equation for a component *i* dissolved in water simplifies to

$$\phi_i^V y_i P = H_{i,w} x_i \qquad (9A7.1\text{-}2)$$

Where:

φ_i^V	=	*the fugacity coefficient of component i in the vapor phase*
y_i	=	*the vapor mole fraction of component i*
P	=	*the total pressure, in psia*
$H_{i,w}$	=	*the Henry's constant for component i dissolved in water (simplified to H)*
x_i	=	*the liquid mole fraction of component i*

Equation (9A7.1-2) can be rearranged to

$$H_{i,w} = \phi_i^V y_i P / x_i \qquad (9A7.1\text{-}3)$$

(The Henry's constant is properly determined by taking the limit of $\varphi_i^V y_i p / x_i$ as $x_i \rightarrow 0$, where the total pressure is the vapor pressure of water. This Henry's constant is a function only of temperature.) To use Equation (9A7.1-3), it will be necessary to calculate φ_i^V. At moderately high pressures ($p < 500$ psia), this can generally be done with the virial equation truncated after the second virial coefficient, but at higher pressures an equation of state that works well for aqueous gas mixtures may have to be used.

If the pressure does not exceed, say, 150 psia, then φ_i^V can be set equal to 1 and

$$H_{i,w} = y_i P / x_i \qquad (9A7.1\_4)$$

If the partial pressure of solute *i*, $y_i P$, is corrected to 1 atm, then $H_{i,w} = 1/x_i$. Which explains why many gas solubility data are tabulated at solute partial pressure of 1 atm (= 14.696 psia). Furthermore, the attractiveness of reporting gas solubility under a gas partial pressure of 1 atm

is such that investigators frequently convert higher pressure data, by using eq. (9A7.1_4) to enable them to report solubilities under a gas partial pressure of 1 atm.

For slightly soluble liquids (x_i < 0.03, as above) and total pressure that does not significantly exceed p_3, the equation used to calculate the Henry's constants is

$$H_{i,w} = \phi_i^{sat} p_i^{sat} / x_i \qquad (9A7.1\text{-}5)$$

Where:

φ_i^{sat} = *the fugacity coefficient of component i at saturation*

p_i^{sat} = *the vapor pressure of component i, in psia*

The vapor pressure of the liquid solutes was generally taken from the public edition of the DIPPR 801 pure-component property database (181.1a), while the fugacity coefficient at saturation was calculated with Lyckman's correlation (128.1a).

Several of the compounds listed in Table 9A7.2 are weak electrolytes; that is, they partially dissociate in aqueous solution. If only a *single* weak electrolyte HA is considered, in aqueous solution it will be present in two forms: the undissociated or molecular HA and the ion A^-. But there will be only molecular HA in the vapor, which will be a function of the molecular HA in aqueous solution. Except in the limit of infinite dilution, the A^- ions can be neglected in the determination of the Henry's constants. However, SO_2, the strongest of the electrolytes in Table 9A7.2, dissociates extensively in aqueous solution to form HSO_3^- ions, and thus only an *apparent* Henry's constant can be determined because the solubility data reflect the presence of both SO_2 and HSO_3^-.

The situation is completely different when a weak base (ammonia) and a weak acid (hydrogen sulfide) are present in the aqueous solution (as they are in sour water strippers). For example, in an equimolar aqueous solution of ammonia and hydrogen sulfide, about 90 percent of these two "weak" electrolytes will be present as NH_4^+ and HS^- ions.

Reliability

Table 9A7.2 lists 18 organic compounds (14 C_1 to C_5 hydrocarbons and 4 organic sulfur compounds) and 18 inorganic elements and compounds. The goodness of fit of the Henry's constant data for these 36 chemical substances with equation (9A7.1-1) is given in two different ways. For 19 of them, Table 9A7.2 reports the percent AAD (average absolute deviation) and bias (see above), while for the other 17 (mostly inorganics) the goodness of fit is given in footnotes by the standard deviation in solubility or in the Henry's constant. The overall percent AAD is 3.1 for 9 hydrocarbons; 5.1 for the 4 organic sulfur compounds; and 7.0 for 6 inorganics.

Literature Sources

Equation 9A7.1-1 was developed by T. J. Edwards, J. Newman, and J. M. Prausnitz (54a). Coefficients were determined by the API Technical Data Book project staff (1996).

Example

Calculate the solubility of hydrogen sulfide in water at 77 °F and 14.696 psia partial pressure of the gas.

Table 9A7.2 reports the Henry's constant at 77 °F that was calculated with Equation (9A7.1-1) and the parameters b_1, b_2, b_3, and b_4: 7848 psia.

Therefore, the solubility of hydrogen sulfide in water at 77 °F and 14.696 partial pressure of the gas is

$$x = yp/H = 14.696/7848$$

$$x = 0.00187$$

Fogg et al. (18.1d) report 0.00185. (At such a mole fraction, the dissociation to HS^- can be totally neglected. Indeed, it can be ignored if $x > 0.000005$.)

Table 9A7.2 – Coefficients for Procedure 9A7.1

Gas	b_1	b_2	b_3	b_4	Temperature Range (°F)	Data Sources		% AAD	%Bias	H/psia @ 77 °F
						No. Points	References			
Alkanes										
methane	371.4189	–23907.78	–51.91445	0.02365728	32 - 482	23	181.1a, 12d	[a]		5.763E+05
ethane	252.1196	–21553.97	–31.65717	---	32 - 340	16	41a, 85a	5.88	0.80	4.335E+05
propane	282.2076	–24055.35	–35.67087	---	32 - 205	31	87a, 109a	2.62	0.06	5.292E+05
n-butane	338.6397	–28786.13	–43.20986	---	32 - 411	18	87a, 121a, 223a	1.40	0.01	6.671E+05
isobutane	239.5986	–20908.64	–29.74307	---	41 - 220	12	87a, 180a	5.13	0.38	8.839E+05
isopentane	719.3265	–56854.46	–95.37794	---	32 - 140	8	136a, 163a, 169a, 171a	0.027	-0.004	1.088E+06
Cyclopropane	216.5690	–18767.11	–27.11853	---	70 - 220	8	92.1a, 93a,214.1a	3.64	0.42	6.950E+04
Alkenes										
ethylene	228.7372	–19139.92	–28.80114	---	32 - 280	36	5.1a, 20a,45a, 94.1a,136a, 147a	[b]		1.706E+05
propylene	259.1928	–22736.25	–32.63232	---	36 - 280	19	10a, 94.1a, 125a	[c]		1.231E+05
1-butene	280.2333	–24524.73	–35.39486	---	100 - 291	5	28a, 124a	0.539	-0.003	1.737E+05
isobutene	261.4429	–22993.67	–32.89045	---	32 - 158	11	103.1a	[d]		1.427E+05
Other Unsaturated Aliphatic Compounds										
1,3-butadiene	246.2075	–21699.47	–30.99567	---	77 - 220	5	136a, 137a, 181a	4.38	0.12	5.720E+04
acetylene	171.7762	–14688.23	–21.40222	---	34 - 158	8	16a, 59.1a, 90.1a	[e]		1.965E+04
methylacetylene	140.9314	–13443.75	–16.96325	---	32 - 220	9	94a, 136a, 200a	4.19	0.15	1.052E+04

Table 9A7.2 – Coefficients for Procedure 9A7.1 (Continued)

Gas	b_1	b_2	b_3	b_4	Temperature Range (°F)	Data Sources		% AAD	%Bias	H/psia @ 77 °F
						No. Points	References			
Organic Sulfur Compounds										
methyl mercaptan	24.90315	-3510.403	-1.661375	---	77 - 212	7	32.2d,33.1d	2.85	0.06	2.751E+03
ethyl mercaptan [f]	264.744	-23144	-33.955	---	122, 176	2	33.1d	3.2	-0.7	3.636E+03
n-propyl mercaptan	504.5375	-42776.87	-66.24951	---	59 - 212	11	11.1d, 29.1d, 33.1d	9.57	0.81	4.564E+03
thiophene	253.4095	-24330.69	-31.89399	---	50 - 392	9	3a, 29.1d	4.93	0.14	2.013E+03
Inorganic Compounds										
ammonia	–129.1167	–1023.3805	23.03971	–0.0208340	32 - 473	21	11d, 32.1d, 53.1d	[g]		1.358E+01
argon [h]	368.02	–23594.7	–51.464	0.023640	32 - 563	63		7.05	1.03	5.801E+05
arsine	157.9622	–13983.61	–19.16938	---	32 - 79	19	32.3d	[i]		9.104E+04
carbon dioxide	139.7316	–13222.61	–16.71023	---	32 - 633	27	15d, 31.2d, 37.1d	[k]		2.346E+04
carbon disulfide	325.5106	–29732.22	–41.47731	---	40 - 400	9	24d	12.07	1.16	1.219E+04
carbon monoxide	187.1706	–14788.63	–23.22799	---	32 - 572	24	32.4d,56.1d	1.82	0.03	8.204E+05
carbonyl sulfide	254.5412	–22465.66	–32.16375	---	32 - 100	10	94.1a, 24d, 85d	3.91	0.11	3.699E+04
chlorine	160.0164	–14212.08	–19.80112	---	50 - 140	11	87.2d	0.73	0.004	8.750E+03
helium [h]	306.02	–17587.5	–42.873	0.020141	32 - 527	50		16.19	10.90	2.157E+06
hydrogen	82.68234	–6368.101	–8.779572	–0.0033572	32 - 662	smoothed	31.1d	[l]		1.016E+06
hydrogen sulfide	58.43341	–8025.971	–4.993226	–0.0058247	32 - 626	smoothed	18.1d	[m]		7.848E+03
mercury	340.1846	–33286.14	–42.8448	---	32 - 248	smoothed	26.1d	[n]		7.081E+03
nitric oxide	183.976	–14821.56	–22.8155	---	32 - 176	9	84d	[o]		4.226E+05
nitrogen	363.6656	–22667.09	–50.99074	0.0244564	32 - 392	smoothed	31.1d	[p]		1.274E+06
nitrous oxide	173.8007	–15989.04	–21.2531	---	32 - 104	smoothed	87.1d	[q]		3.365E+04
oxygen	205.158	–15380.51	–26.34913	0.0046410	32 - 662	smoothed	31.1d	[r]		6.438E+05
phosphine	170.5979	–14823.29	–20.91652	---	77 - 122	5	70.1d	[s]		9.958E+04
sulfur dioxide	57.47473	–8235.94	–5.68545	---	41 - 230	smoothed	87.2d	[t]		5.977E+02

Procedure 9A7.3 – Equilibrium Concentrations of Sour Gas Systems in Water

Discussion

This procedure was last updated in 1999. The following equations are used to calculate the equilibrium concentration for binary and ternary systems of ammonia and hydrogen sulfide gases in water. Binary system equilibrium concentrations can be calculated using Equation (9A7.3-1). Ternary system equilibrium concentrations can be calculated iteratively using Equation (9A7.3-2). Inputs needed include operating temperature in °R and the partial pressure of the selected components mmHg.

$$log(PP) = A_1 * PPM^2 + A_2 * PPM + A_3 T + A_4 \qquad (9A7.3\text{-}1)$$

$$log(PP) = C_1 * PPM^2 + C_2 * PPM + C_3 * Z_M + C_4 \qquad (9A7.3\text{-}2)$$

Where:

PP	=	*Partial Pressure (mmHg)*
PPM	=	*Log (parts per million wt.)*
T	=	*Temperature (°R)*
Z_M	=	*Function of molar ratio. (See special comments)*

Procedure

BINARY SYSTEMS

Step 1: *Read the constant A_1, A_2, A_3 and A_4 for given component from Table 9A7.4.*

Step 2: *Calculate the weight concentration in parts per million at the operating temperature and partial pressure of the gas.*

TERNARY SYSTEMS

Step 1: *Obtain the operating temperature and initial estimates of partial pressure for NH_3 and H_2S.*

Step 2: *Calculate the molar ratio of ammonia to hydrogen sulfide.*

Step 3: *Select and calculate the Z term based on the temperature and molar ratio.*

Step 4: *Using the partial pressure, Z term and appropriate constants from Table 9A7.4 calculate the partial pressure of the selected component from Equation 9A7.3-2.*

Step 5: *Repeat Steps 2-4 for the other component.*

Step 6: *Repeat Steps 2-6 until the partial pressures converge.*

Comments on Procedure 9A7.3

Purpose

This procedure is given for estimating the equilibrium concentrations of ammonia and hydrogen sulfide in water from the system and partial pressure of the gas.

Limitations

This procedure is limited to a temperature range of 80–300 °F and to concentrations below 10% for the gas. Extrapolation beyond these limits is not recommended.

Reliability

Within the limits of the correlation, the average errors for Equation (9A7.3-1) and Equation (9A7.3-2) are 7.7% and 8.4% respectively. The biases for the two equations are –0.4% and –0.5% respectively.

Special Comments

The procedure will interpolate between the temperatures listed in Table 9A7.4 for the ternary system by using an inverse lever rule.

The Z_M term in equation 9A7.3-2 is a function of the molar ratio. The actual function is determined from Table 9A7.4. The possible functions are:

$$\frac{1}{M^2}$$

$$log(M)$$

$$1 - \frac{M^2}{6} + \frac{M^4}{120} \; or \frac{sin(M)}{M}$$

Where:

M = *molar ratio of ammonia to hydrogen sulfide*

Literature Sources

This procedure was correlated from a method developed by S.A. Newman*, Hydrocarbon Processing* **70**[9,10,11] (1991).

Examples

BINARY SYSTEMS

Find the equilibrium concentration of ammonia in water at 248 °F and partial pressure of 3.54 psia for ammonia.

From Equation (9A7.3-1) and the constants in Table 9A7.4, the weight concentration for ammonia is 10035 ppm at the operating conditions. The experimental concentration is 8770 ppm by weight (229a).

TERNARY SYSTEM

Find the concentration of ammonia and hydrogen sulfide in water at 248 °F when the partial pressure of hydrogen sulfide is 82.5 mmHg and the weight concentration is 7000 ppm.

From Equation (9A7.3-2) and the parameters in Table 9A7.4, the molar ratio of ammonia to hydrogen sulfide in water is calculated to be 5.57. The experimental molar ratio is 4.8 (81d).

Table 9A7.4 – Parameters of Equations (9A7.3-1,2): Equilibrium Concentrations of Sour Gas Systems in Water

BINARY PARAMETERS							
Component				A_1	A_2	A_3	A_4
ammonia				0.01129	0.9568	0.00719	-6.83498
hydrogen sulfide				-0.00322	1.0318	0.00248	-1.95729
TERNARY PARAMETERS							
Component	**Temp. (°R)**	**Molar Ratio**	Z_M	C_1	C_2	C_3	C_4
ammonia	537.67	.7-20	1	0.02998	0.838848	-1.34384	-2.8802
ammonia	537.67	.1-.7	2	0.13652	0.074081	1.12893	-3.8683
hydrogen sulfide	537.67	.1-1	3	-0.00562	1.028528	8.33185	-8.9175
hydrogen sulfide	537.67	1.4-4.0	2	0.00227	0.980646	-2.82752	-2.3105
hydrogen sulfide	537.67	4.-50	2	0.00138	0.881842	-1.08346	-2.7605
ammonia	559.67	.7-20	1	0.03894	0.775221	-1.17860	-2.5972
ammonia	559.67	.1-.7	2	0.06415	0.659240	1.24672	-4.5124
hydrogen sulfide	559.67	.1-1	3	-0.00487	1.025371	7.46512	-7.9480
hydrogen sulfide	559.67	1.1-3	2	0.01018	0.915687	-2.65953	-1.9435
hydrogen sulfide	559.67	4-50	2	0.00668	0.849756	-1.10875	-2.4133
ammonia	579.67	.7-20	1	0.02393	0.881656	-1.08692	-2.5668
ammonia	579.67	.1-.7	2	0.09581	0.420378	1.30988	-3.7033
hydrogen sulfide	579.67	.1-1	3	0.00308	0.976347	6.81079	-7.1893
hydrogen sulfide	579.67	1.1-3	2	0.00562	0.932481	-2.48535	-1.6691
hydrogen sulfide	579.67	4-50	2	0.01577	0.778382	-1.07217	-1.9946
ammonia	609.67	-.7-10	1	0.02580	0.856844	-0.90996	-2.2738
ammonia	609.67	.1-.7	2	0.07081	0.625739	1.23245	-3.5797
hydrogen sulfide	609.67	.1-.9	2	-0.02064	1.090006	-0.66045	-1.0928
hydrogen sulfide	609.67	1-2	2	0.00144	0.961073	-3.00981	-1.2917
hydrogen sulfide	609.67	3-50	2	0.01306	0.813499	-1.15162	-1.5845
ammonia	659.67	1.6-20	2	0.06548	0.621031	0.24106	-1.9006
ammonia	659.67	1.1-1.5	2	0.05838	0.683411	1.95035	-2.4470
ammonia	659.67	.5-1	2	-0.07626	1.462759	2.57458	-3.5185
hydrogen sulfide	659.67	1.5-.5	2	0.00398	0.997000	-1.95892	-1.1374
hydrogen sulfide	659.67	1.6-20	2	-0.00651	1.037056	-1.24395	-1.4799
ammonia	679.67	1.5-20	2	0.05840	0.647857	0.28668	-1.8320
ammonia	679.67	1-1.4	2	0.02447	0.864904	2.60250	-2.5186
ammoni	679.67	.5-.9	2	-0.08280	1.479719	2.26608	-3.3007
hydrogen sulfide	679.67	.5-1.5	2	0.00892	0.957002	-1.84465	-0.9934
hydrogen sulfide	679.67	1.6-20	2	0.00674	0.910272	-1.16113	-1.0837
ammonia	699.67	1.6-20	2	0.04542	0.756870	0.18305	-1.8041
ammonia	699.67	1-1.5	2	0.03659	0.790904	2.00739	-2.2410
ammonia	699.67	.5-.9	2	-0.07386	1.445958	1.79890	-3.1476
hydrogen sulfide	699.67	.5-20	2	0.00000	1.002832	-1.40994	-0.9558
ammonia	719.67	1.6-20	2	0.04603	0.728930	0.17864	-1.5652
ammonia	719.67	1.5-1	2	0.03493	0.796292	1.69221	-2.0369
ammonia	719.67	.5-.9	2	-0.07354	1.437440	1.73508	-2.8916
hydrogen sulfide	719.67	.5-1.5	2	0.00871	0.964568	-1.44142	-0.7861
hydrogen sulfide	719.67	1.6-20	2	-0.01035	1.054256	-1.22074	-0.9966
ammonia	739.67	1.5-20	2	0.04484	0.728061	0.25132	-1.5543
ammonia	739.67	.9-1.4	2	0.00193	0.998553	1.87924	-2.1925
ammonia	739.67	.5-.8	2	-0.06773	1.391080	1.68263	-2.6696
hydrogen sulfide	739.67	.5-20	2	0.00000	1.000692	-1.23871	-0.7932
PARAMETERS FOR MOLAR RATIO RANGED (Z_M)							
1. $\frac{1}{M^2}$			2. $\log(M)$			3. $1-\frac{M^2}{6}+\frac{M^4}{120}$	

9A8 pH of Nonhydrocarbon Gases in Water

Procedure 9A8.1 – pH of Ammonia and Hydrogen Sulfide Gases in Water

Discussion

This procedure was last updated in 1999. The following equations are to be used to calculate the pH for binary and ternary systems of ammonia and hydrogen sulfide gases in water. The pH for a binary system can be calculated using Equation (9A8.1-1). Inputs for binary systems include the component of choice, the operating temperature and the weight concentration of the chosen component in parts per million. The pH for a ternary system can be calculated using Equation (9A8.1-2). Inputs for ternary systems include the operating temperature and the molar ratio of ammonia to hydrogen sulfide in water.

$$pH = A_1 * PPM + A_2 * T + A_3 \qquad (9A8.1\text{-}1)$$

$$log(pH) = C_1 * log[log(M)] + C_2 * log(M) + C_3 * T + C_4 \qquad (9A8.1\text{-}2)$$

Where:

PPM	=	*Log (Parts per million wt.)*
T	=	*Temperature °R*
M	=	*Moles NH_3/moles H_2S in solution*

Procedure

Step 1: *Select the appropriate equation based on the system composition: Equation (9A8.1-1) for binary systems; Equation (9A8.1-2) for ternary systems.*

Step 2: *Obtain the related coefficients from Table 9A8.2.*

Step 3: *From the selected Equation, calculate the pH from the operating temperature and either the weight concentration (in ppm wt) for binary systems or the ammonia/hydrogen sulfide molar ratio for ternary systems.*

Comments on Procedure 9A8.1

Purpose

This procedure is given for estimating the system pH of ammonia and hydrogen sulfide in water from the temperature and the equilibrium concentration of the gases.

Limitations

This procedure is limited to concentrations below 10 wt% for the gases. For binary systems, the temperature range is limited to 80–300 °F and 80–200 °F for ammonia/water and hydrogen sulfide/water systems, respectively. For ternary systems, the temperature range is 80–150 °F. Extrapolation beyond these limits is not recommended.

Reliability

The reliability of the pH values has been found to be within ±5 percent.

Literature Source

This procedure was correlated from a procedure developed by S. A. Newman, *Hydrocarbon Processing*, **70** [11] 139 (1991).

Example

Find the pH of an ammonia/hydrogen sulfide/water system at an operating temperature of 80 °F with an ammonia/hydrogen sulfide molar ratio of 2.0.

From Equation (9A8.1-2), the pH is calculated to be 8.6 at the operating conditions. An experimental value for the pH at these conditions is 9.73 (79d).

Table 9A8.2 – Parameters for Equations (9A8.1-1 and 9A8.1-2)

Binary Parameters			
	A_1	A_2	A_3
ammonia	0.480	–0.0106	15.236
hydrogen sulfide	–0.505	–0.0019	6.807
Ternary Parameters			
C1 = –0.0084		C2 = 0.1129	
C3 = –0.00032		C4 = 1.0689	

9B Gas Hydrates

9B1 Graphical Procedures for Prediction of Gas Hydrate Equilibria

Figure 9B1.1 – Hydrate Pressure-Temperature Equilibria

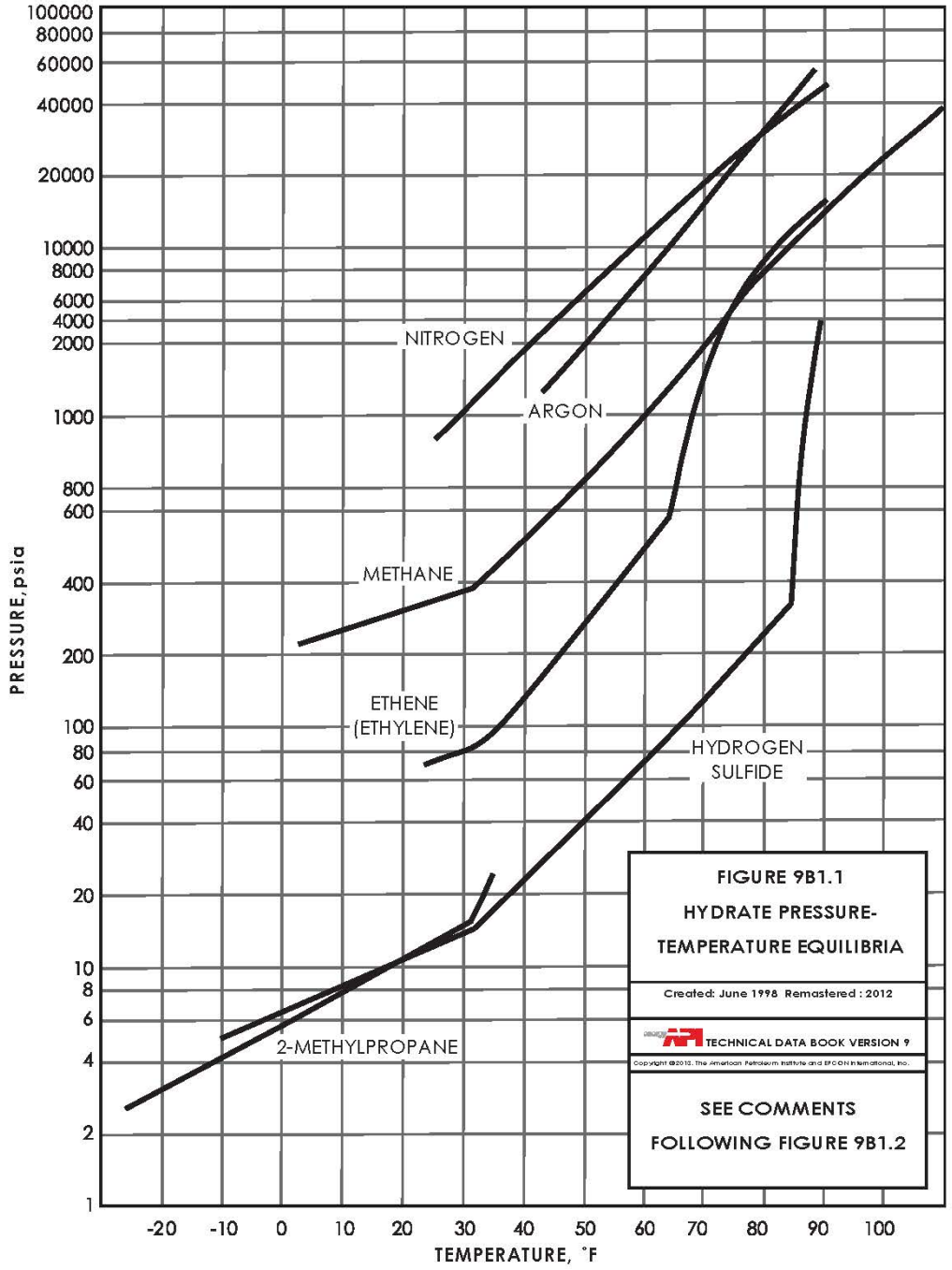
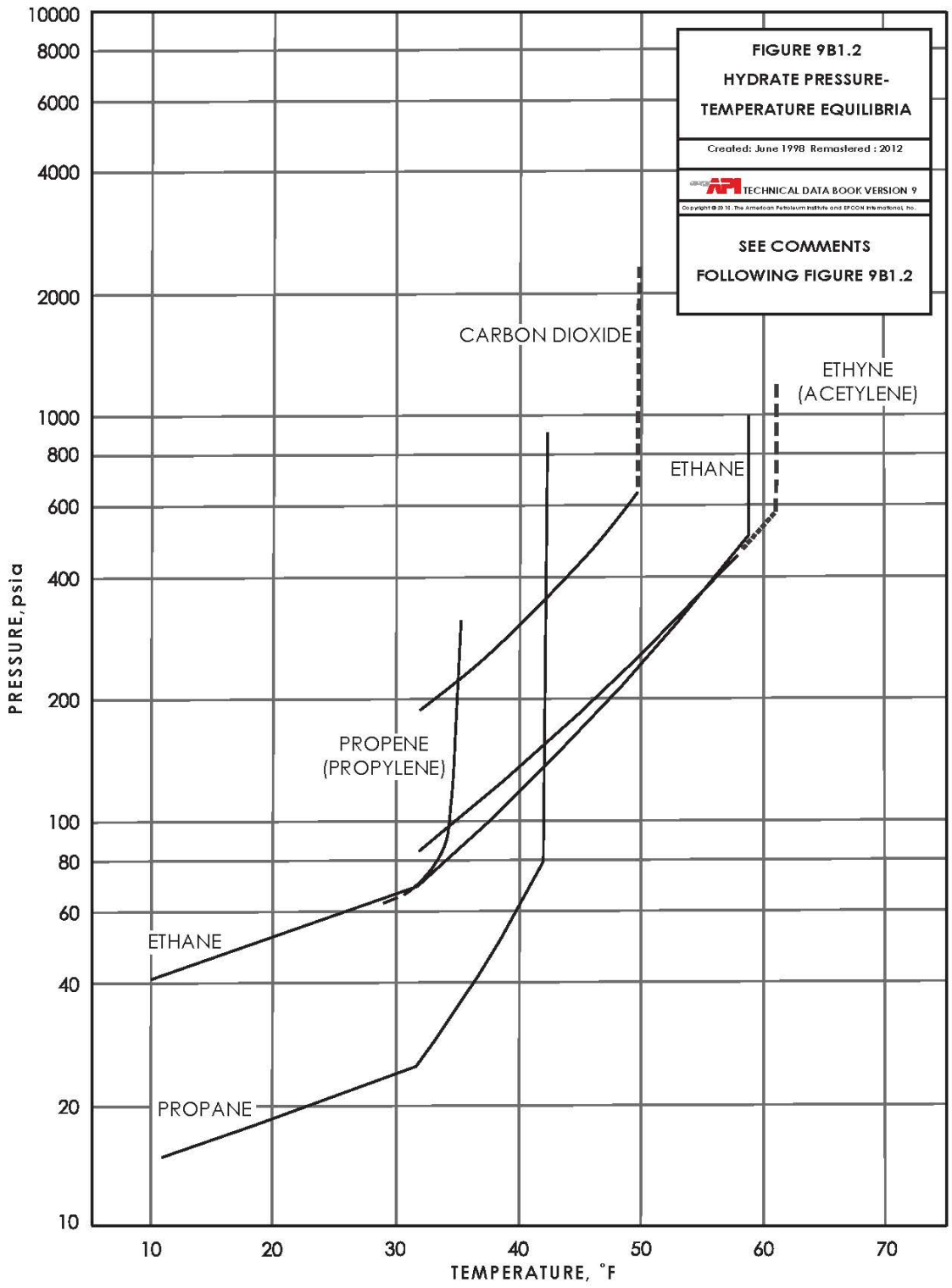


Figure 9B1.2 – Hydrate Pressure-Temperature Equilibria



Comments on Figures 9B1.1 and 9B1.2

Purpose

This procedure was last updated in 1999. The curves in these figures indicate the pressure-temperature regions in which gas hydrate formation is favored (above and to the left of the appropriate curve).

Limitations

Equilibrium conditions are shown in the figures; however, since hydrate systems typically exhibit metastable tendencies, a metastable hydrate phase can exist far out of the hydrate region. Conversely, hydrate formation will not always occur in the region in which formation is favored.

Reliability

The figures show the equilibrium hydrate conditions to within 2 percent of the pressure.

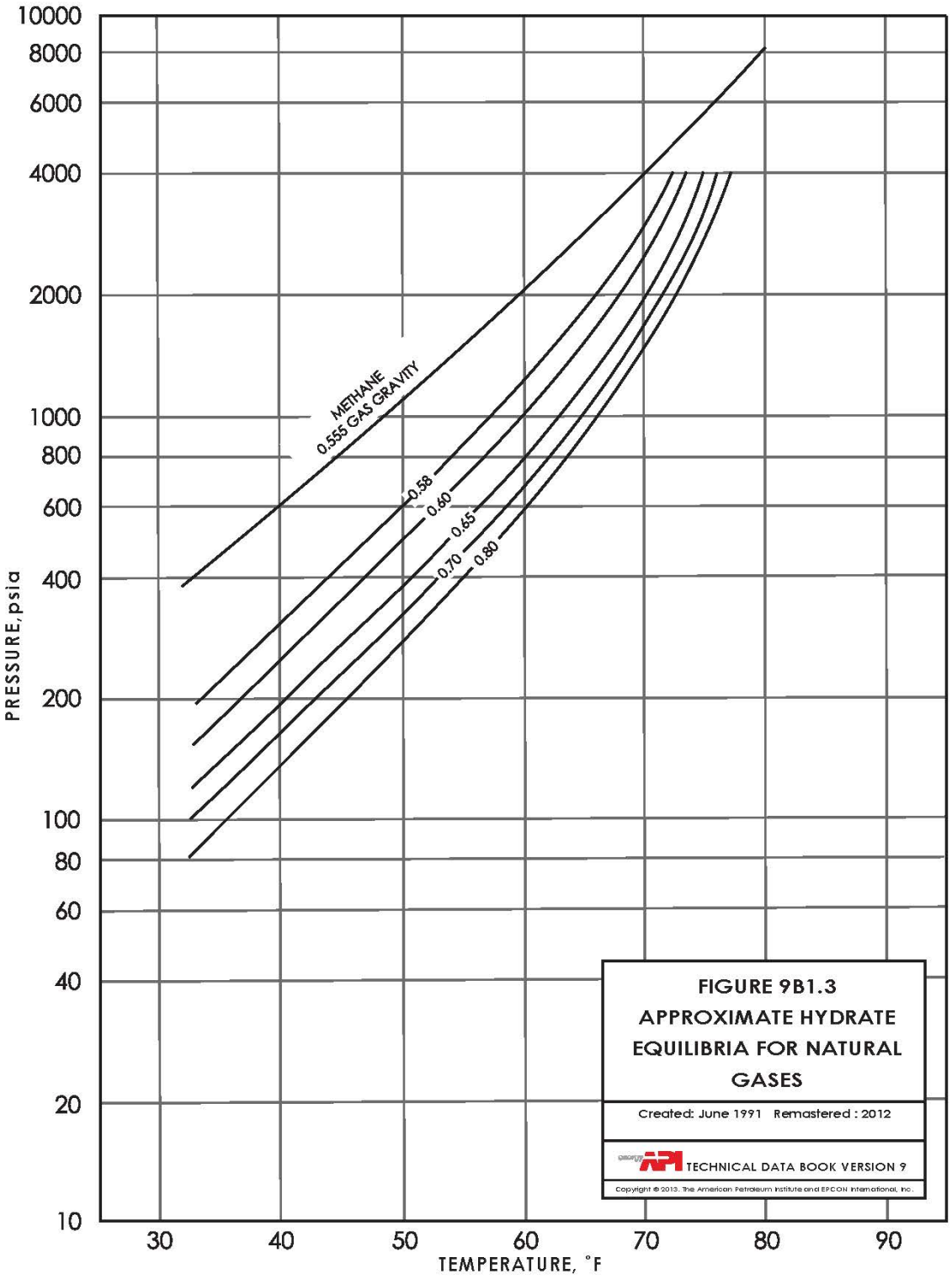
Special Comments

The discontinuities on the lines correspond to changes in phase of the non-hydrate phases. For multicomponent systems, hydrate formation conditions determined by Procedure 9B2.1 are recommended. Small amounts of impurities can exert a very strong influence on hydrate formation conditions.

Literature Sources

Sources of hydrate equilibrium data for these figures are listed in Table 9-0.6.

Figure 9B1.3 – Approximate Hydrate Equilibria for Natural Gases



Comments on Figure 9B1.3

Purpose

This procedure was last updated in 1999. The curves in this figure indicate the pressure-temperature regions in which gas hydrate formation is favored (above and to the left of the appropriate curve). Each curve applies to a different specific gravity (air = 1.0).

Limitations

Applicability is limited to natural gases containing no more than 3 mole percent of nitrogen, carbon dioxide or hydrogen sulfide and no more than 7 percent of hydrocarbons heavier than ethane.

Reliability

For hydrate equilibria, specific gravity does not satisfactorily characterize a natural gas. As a result, an average error in pressure of 10 percent and a maximum of 40 percent occurs between figures and published experimental data for gases that do not contain appreciable amounts of nitrogen, carbon dioxide, hydrogen sulfide and hydrocarbons of molecular weights greater than ethane.

Special Comments

In view of its low reliability, the figure is recommended as a guide. More accurate formation conditions can be predicted using Procedure 9B2.1.

Literature Sources

Sources of hydrate equilibrium data for this figure are listed in Table 9-0.6.

Figure 9B1.4 – Permissible Expansion of a 0.6 Gravity Natural Gas Without Hydrate Formation

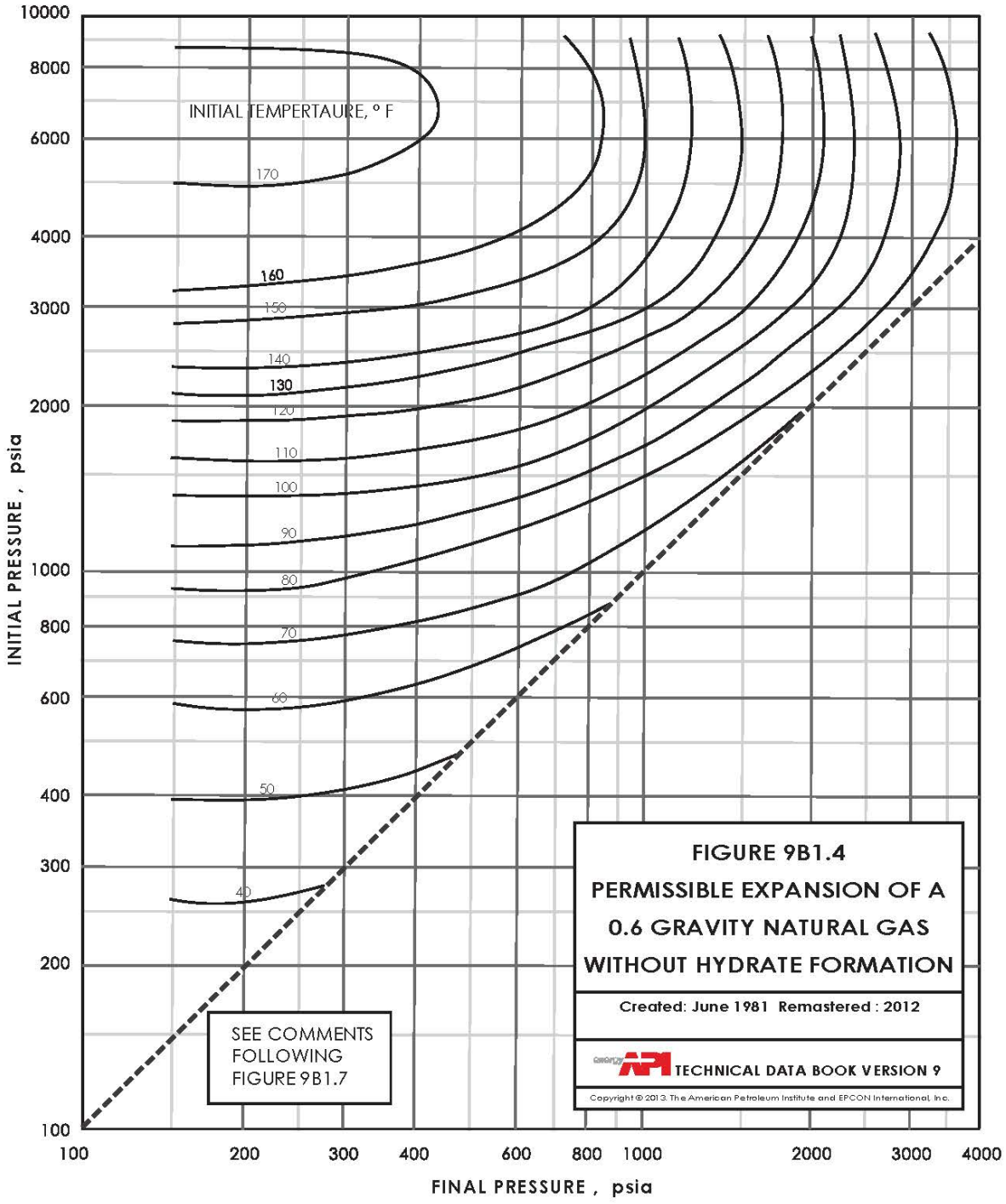


Figure 9B1.5 – Permissible Expansion of a 0.7 Gravity Natural Gas Without Hydrate Formation

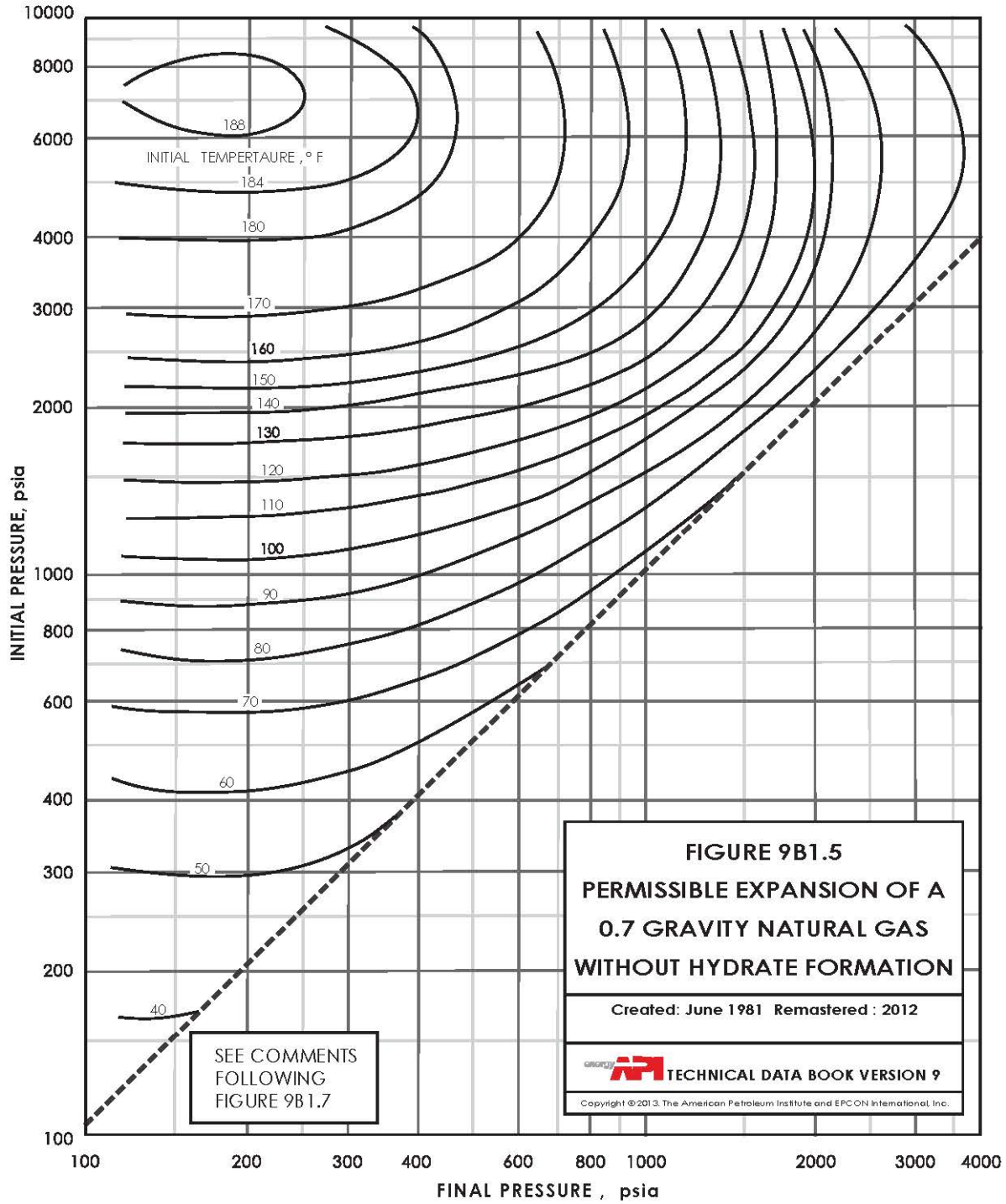


Figure 9B1.6 – Permissible Expansion of a 0.8 Gravity Natural Gas Without Hydrate Formation
(1999)

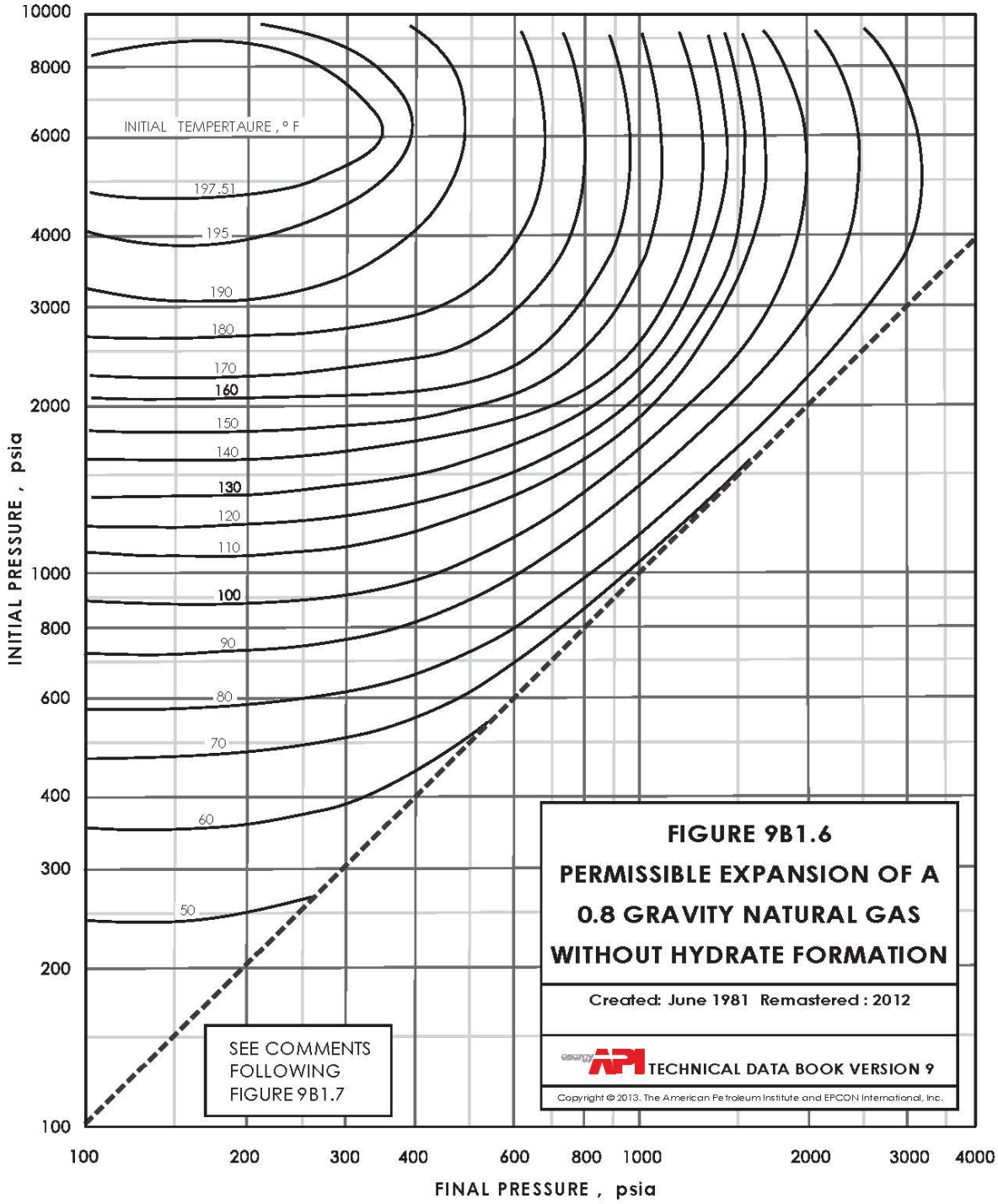
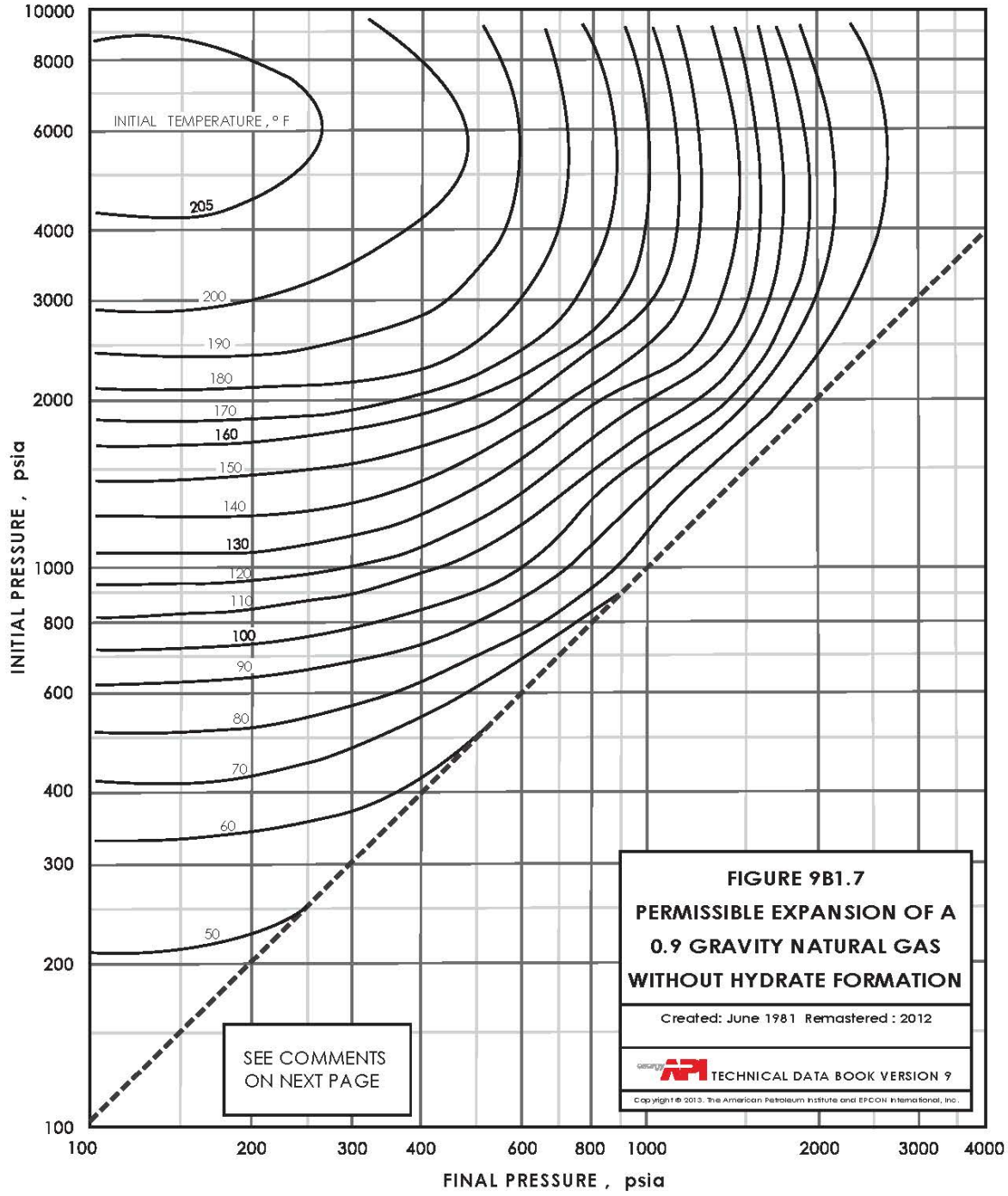


Figure 9B1.7 – Permissible Expansion of a 0.9 Gravity Natural Gas Without Hydrate Formation



Comments on Figures 9B1.4 through 9B1.7

Purpose

This procedure was last updated in 1999. The figures show the amount of expansion that can be permitted in natural gases before hydrate formation occurs.

Limitations

The charts are limited to natural gases that are predominantly methane.

Reliability

For mixtures that are predominantly methane, an average error of 10 percent is expected. Higher errors will occur when appreciable quantities of nitrogen or hydrocarbons heavier than ethane are present.

Special Comments

For gases of specific gravities other than 0.6, 0.7, 0.8 and 0.9 (air = 1.0), linear interpolation between the figures is recommended.

Literature Source

The figures were redrawn from Katz, *Trans. AIME* **160** 140 (1945).

Examples

A. If natural gas of 0.8 gravity initially at 1000 pounds per square inch absolute and 100 °F is expanded adiabatically, at what pressure will hydrates first appear?

   In figure 9B1.6 read the final pressure from the intersection of the 1000 pounds per square inch absolute initial pressure line and the 100 °F isotherm. The gas may not be expanded to pressure below 440 pounds per square inch absolute without danger of hydrate formation.

B. If the gas in Example A is initially at 1000 pounds per square inch absolute and 110 °F, at what pressure will hydrates form from an adiabatic expansion?

   The 1000 pounds per square inch absolute initial pressure line in Figure 9B1.6 does not intersect with the 110 °F isotherm which indicates that the adiabatic expansion will not cool the gas enough to form hydrates.

C. A gas of 0.8 gravity is expanded adiabatically from 1500 pounds per square inch absolute to 600 pounds per square inch absolute. What is the minimum initial gas temperature be to avoid hydrate formation?

   The intersection of the 1500 pounds per square inch absolute initial pressure line and the 600 pounds per square inch absolute final pressure line occurs at 120 °F in Figure 9B1.6. For an initial temperature below 120 °F, a hydrate will form, but for temperatures greater than 120 °F, the gas will not be cooled sufficiently by this expansion to cause hydrate formation.

9B2 Computer Method for Prediction of Gas Hydrate Equlibria

Procedure 9B2.1 – Computer Method for Prediction of Gas Hydrate Formation Conditions

Discussion

This procedure was last updated in 2005. Formation conditions of hydrates from mixtures of hydrocarbons and related gases can be estimated using the Parrish-Prausnitz correlation based on a theory developed by van der Waals and Platteeuw. This theory uses a model similar to the Langmuir model for gas adsorption and contains the basic statistical thermodynamic equations for gas hydrates. An alternative method for prediction of gas hydrate formation has been developed by E. Dendy Sloan at the Colorado School of Mines.

Three phases coexist in the gas hydrate system: (1) the hydrate phase, (2) the gas phase whose composition needs to be known on a water-free basis, and (3) an ice phase (below 32 °F) or a water-rich liquid phase (above 32 °F). At equilibrium, the chemical potential of water in the hydrate phase equals that in each of the other coexisting phases. Therefore, if ice is present,

$$\mu_w^H(T,P,\theta) = \mu_w^\alpha(T,P) \qquad (9B2.1\text{-}1)$$

or if liquid water is present,

$$\mu_w^H(T,P,\theta) = \mu_w^L(T,P) + RT\ ln\ x_w \qquad (9B2.1\text{-}2)$$

Where:

$\mu_w^H(T,P,\theta)$ = *chemical potential of water in hydrate phase*

$\mu_w^\alpha(T,P)$ = *chemical potential of ice*

$\mu_w^L(T,P)$ = *chemical potential of pure water*

x_w = *mole fraction of water in water-rich liquid phase (very close to unity)*

According to the theory of van der Waals and Platteeuw, the difference between the chemical potential of water in the empty hydrate lattice and that in the filled lattice is:

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H = -RT\sum_m \upsilon_m\ ln\left(1 - \sum_j \theta_{mj}\right) \qquad (9B2.1\text{-}3)$$

Where:

μ_w^β = *chemical potential of water in empty hydrate lattice*

μ_w^H = *chemical potential of water in filled hydrate lattice*

υ_m = *number of Type m cavities per water molecule in the lattice*

θ_{mj} = *fraction of Type m cavities occupied by Gas Component j*

$$\theta_{mj} = C_{mj} f_j \Big/ \left(1 + \sum_l C_{ml} f_l\right) \qquad \textit{(9B2.1-4)}$$

Where:

C_{mj} = *Langmuir constant for Component j and Cavity Type m*

f_j = *fugacity of Component j in the gas phase*

Because of equilibrium conditions, the following chemical potential differences are defined:

$$\Delta\mu_w^\alpha = \mu_w^\beta - \mu_w^\alpha \qquad \textit{(9B2.1-5)}$$

$$\Delta\mu_w^L = \mu_w^\beta - \mu_w^L \qquad \textit{(9B2.1-6)}$$

Where:

$\Delta\mu_w^\alpha$ = *chemical potential difference between empty hydrate lattice and ice*

$\Delta\mu_w^L$ = *chemical potential difference between empty hydrate lattice and liquid water*

If ice is present, Equation (9B2.1-5) is equal to Equation (9B2.1-3). If liquid water is present, Equations (9B2.1-3) and (9B2.1-6) are equal.

The hydrate formation conditions may now be determined by computing a calculated chemical potential difference and an experimental chemical potential difference. Using an iterative process, equations for both quantities are solved simultaneously.

A. Calculated Chemical Potential Difference

The calculated chemical potential difference is given by

$$\Delta\mu_w^L = RT \sum_m \upsilon_m \, ln\left(1 + \sum_j C_{mj}\phi_j y_i P\right) + RT \, ln \, x_w \qquad \textit{(9B2.1-7)}$$

if water is present, or by

$$\Delta\mu_w^L = RT \sum_m \upsilon_m \, ln\left(1 + \sum_j C_{mj}\phi_j y_i P\right) \qquad \textit{(9B2.1-8)}$$

if ice is present.

Where:

v_m	=	*the number of Type m cavities per water molecule in the lattice*
y_j	=	*mole fraction of Component j in the gas phase on a water-free basis*
ϕ_j	=	*fugacity coefficient of Component j in the gas phase*
C_{mj}	=	*Langmuir constant for Component j and Type m cavity*

The Langmuir constant is given by

$$C(T) = \frac{4\pi}{kT}\int_0^\infty exp\left[-\frac{w(r)}{kT}\right]r^2 dr \qquad \textit{(9B2.1-9)}$$

Where:

T	=	*absolute temperature*
k	=	*Boltzmann's constant*
$w(r)$	=	*spherically symmetric cell potential*

$$w(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right] \qquad \textit{(9B2.1-10)}$$

$$\delta^N = \left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right]/N \;\; for\; N = 4, 5, 10, 11. \qquad \textit{(9B2.1-11)}$$

Where:

z	=	*coordination number*
R	=	*cell radius of the cavity*
ε	=	*characteristic energy of the hydrate-gas interactions*
a	=	*spherical core radius*
$\sigma + 2a$	=	*collision diameter*

2*a*, *σ*, and ε/k are known as the Kihara parameters.

B. Experimental Chemical Potential Difference

The experimental chemical potential difference is determined in two steps by using a reference hydrate. The dissociation pressure of the reference hydrate P_R at temperature of the system, *T*, is calculated using equation (9B2.1-12)

$$ln\, P_R = A_R + B_R/T + C_R\, ln\, T \qquad \textit{(9B2.1-12)}$$

Where:

A_R, B_R, C_R	=	*constants dependent on the reference hydrate, given in Table 9B2.5.*

The chemical potential difference for the reference hydrate at this condition is calculated using either equation (9B2.1-13) or equation (9B2.1-14). If ice is present,

$$\frac{\Delta\mu_w^L(T,P_R)}{RT} = \frac{\Delta\mu_w^\alpha(T_o,P_o)}{RT_o} - \int_{T_0}^{T}\frac{\Delta h_w^\alpha}{RT^2}dT + \int_{T_0}^{T}\frac{\Delta v_w^\alpha}{RT}\left(\frac{dP}{dT}\right)dT \qquad (9B2.1\text{-}13)$$

If liquid water is present,

$$\frac{\Delta\mu_w^L(T,P_R)}{RT} = \frac{\Delta\mu_w^L(T_o,P_o)}{RT_o} - \int_{T_0}^{T}\frac{\Delta h_w^\alpha + \Delta h_w^f}{RT^2}dT + \int_{T_0}^{T}\left(\frac{\Delta v_w^\alpha + \Delta v_w^f}{RT}\right)\left(\frac{dP}{dT}\right)dT \qquad (9B2.1\text{-}14)$$

Where:

T_0	=	*the ice point temperature of the reference hydrate*
P_0	=	*the dissociation pressure of the reference hydrate at T_o*
Δh_w^α	=	*molar difference in enthalpy between the empty hydrate lattice and ice*
Δv_w^α	=	*molar difference in volume between the empty hydrate lattice and ice*
Δh_w^f	=	*heat of fusion*
Δv_w^f	=	*change of volume due to fusion*
dP/dT	=	*slope of pressure-temperature curve for the reference hydrate*

Finally, the experimental chemical potential is calculated by equation (9B2.1-15) or (9B2.1-16).

If ice is present,

$$\Delta\mu_w^\alpha(T,P) = \Delta\mu_w^\alpha(T,P_R) + \Delta v_w^\alpha(P - P_R) \qquad (9B2.1\text{-}15)$$

If water is present,

$$\Delta\mu_w^L(T,P) = \Delta\mu_w^L(T,P_R) + \left(\Delta v_w^\alpha + \Delta v_w^f\right)(P - P_R) \qquad (9B2.1\text{-}16)$$

C. Composition

The composition of the hydrate phase may be calculated by equation (9B2.1-17).

$$Y_j = \frac{\sum_m \upsilon_m \theta_{mj}}{\sum_m \upsilon_m \sum_l \theta_{ml}} \qquad (9B2.1\text{-}17)$$

Where:

Y_j = *mole fraction of Component j in the hydrate phase on a water-free basis.*

Procedure

A. Procedure for Pressure Prediction

Step1: *For each component, obtain the critical temperature, pressure and acentric factor from the pure component properties tables, the Soave equation-of-state parameters from Chapter 8 and the solubility data from Chapter 9.*

Step 2: *Enter the temperature and the composition of the gas phase on a water-free basis.*

Step 3: *Check Table 9B2.3 to determine if T is higher than the upper quadruple point of the hydrate-forming gases. If so, no hydrate will form and the procedure is stopped.*

Step 4: *Estimate the formation pressure. A good estimate would be the formation pressure of the reference hydrate at the given temperature from equation (9B2.1-12).*

Step 5: *Determine which hydrate structure is formed. If a Structure II-forming gas is present, assume Structure II is formed. If not, assume Structure I is formed.*

Step 6: *Calculate the Langmuir constants using equations (9B2.1-9) through (9B2.1-11) and Table 9B2.4.*

Step 7: *Calculate the experimental chemical potential difference at the reference pressure using equation (9B2.1-13) or (9B2.1-14).*

Step 8: *Calculate the fugacity coefficients of the gases and the mole faction of water in the water-rich liquid phase, if applicable.*

Step 9: *Calculate a new pressure by solving equation (9B2.1-7) or (9B2.1-8) and equation (9B2.1-15) or (9B2.1-16) simultaneously. If the new pressure is not equal to the old pressure, re-estimate the pressure and return to Step 8.*

Step 10: *If only the structure assumed in Step 5 is formed, go to Step 12. If Structure II was assumed, save the answer, assume Structure I will form and repeat Steps 6 through 9 until the correct pressure is determined.*

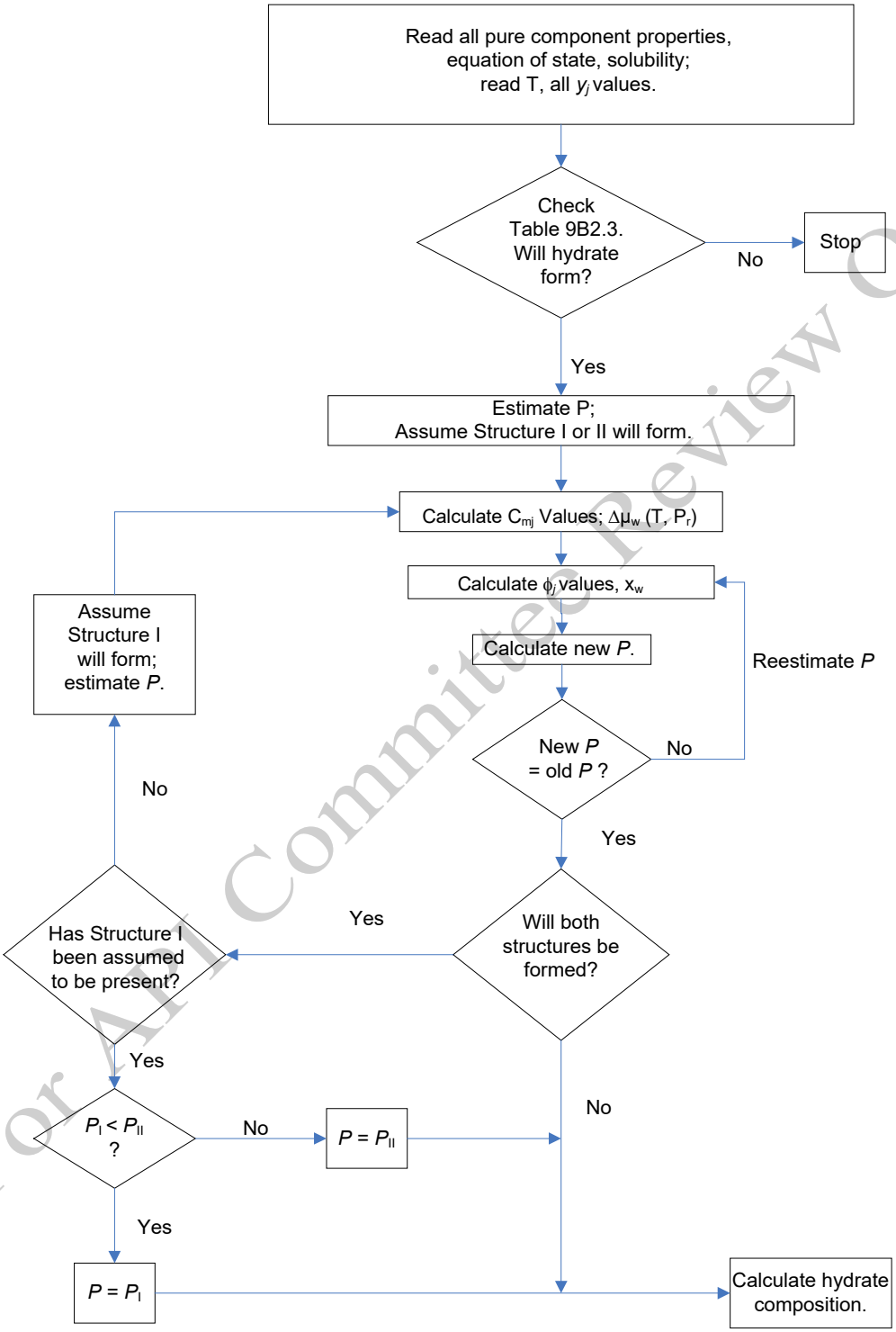
Step 11: *Compare the two pressures. If they are equal, both hydrate structures are formed. If they are not equal, the lower pressure is correct and the structure associated with that pressure will be formed.*

Step 12: *Calculate the hydrate phase composition if desired, using equation (9B2.1-17).*

B. Procedure for Temperature Prediction

Follow the same procedure for pressure prediction, except enter an estimated rather than an experimental temperature. Adjust the temperature each time through the iteration until the calculated pressure equals the given pressure.

Flow Diagram for Prediction of Gas Hydrate Formation Pressure



Comments on Procedure 9B2.1

Purpose

This procedure is to be used to estimate the formation conditions of hydrates formed from hydrocarbons and related gases. The vapor-phase composition on a water-free basis needs to be known. The procedure is used to estimate the hydrate formation pressure at a given temperature or the formation temperature at a given pressure. The hydrate-phase composition on a water-free basis may also be computed using this procedure. The parameters are given in Tables 9B2.2 through 9B2.6.

Limitations

This procedure is basically limited to small hydrocarbons and the nonhydrocarbon hydrate formers - nitrogen, carbon dioxide and hydrogen sulfide. Non-hydrate formers, such as hydrogen and hydrocarbons heavier than and including *n* -butane, may also be present and are treated simply as components of the gas mixture.

The procedure is applicable to mixtures of water, hydrocarbons and the related nonhydrocarbons, which exhibit one vapor phase, one water-rich liquid phase and the hydrate phase. It cannot be used for fully condensed systems.

The correlation has been tested against nine pure-component and 25 multicomponent systems. (A binary mixture of water and a hydrate former is considered a pure-component system.) The procedure is applicable to hydrocarbon and hydrogen sulfide pure-component systems but not to nitrogen and carbon dioxide systems. It is most reliable for multicomponent systems in which the concentrations of the nonhydrocarbons are less than about 50 percent. The correlation is most accurate at pressures up to about 10,000 pounds per square inch absolute above which convergence is slow and not always achieved.

Because of the complex nature of the procedure, the convergence routine used is very important and may influence the success or failure of the computer program. Several different techniques may be required to guarantee convergence.

Based on limited data, the procedure is usually reliable for calculating hydrate phase composition. However, components whose gas-phase compositions are less than 20 percent are subject to larger uncertainty.

Reliability

For pressure prediction in pure component systems, an average error of 29 percent can be expected, excluding isobutane. The error in pressure prediction for isobutane is 120 percent. The average error om of temperature prediction for pure component systems is less than 10 °F.

For multicomponent systems, an average error of 25 percent can be expected for pressure prediction. An average error in temperature prediction of 3.8 °F may be expected.

Use this procedure with caution for the calculation of hydrate phase composition and *K* values, since insufficient data are available to predict the expected error.

Special Comments

Ongoing studies are being done to further improve the Kihara parameters in Table 9B2.4. The user is advised to refer to current literature to obtain the most recent values for those parameters.

Literature Source

This procedure is basically from W. R. Parrish and J. M. Prausnitz, *Ind. Eng. Chem. Proc. Des. Develop.* **11** 26 (1972) and has been modified and adapted for use in this book.

Table 9B2.2 – Physical Properties of Hydrate Lattice

	Structure I	Structure II
Ideal Composition[a]	$M_1 \cdot 3M_2 \cdot 32H_2O$	$M_1 \cdot 2M_2 \cdot 17H_2O$
Number of water molecules or unit cell	46	136
Number of cavities per unit cell		
Small	2	16
Large	6	8
Cell diameter, angstroms		
Small	7.90	7.82
Large	8.60	9.46
Coordination number		
Small	20	20
Large	24	28

[a] Hydrate composition if large molecules M_1 occupy all the large cavities and if small molecules M_2 occupy all the small cavities.

Table 9B2.3 – Upper Quadruple Point Conditions for Hydrates of Pure Gases

Gas	Structure Formed	Upper Quadruple Point	
		T (°F)	P (psia)
methane [a]	1	–	–
ethane	1	57.6	479.1
propane	2	41.5	90.8
isobutane	2	35.4	24.2
cyclopropane [b]	1, 2	61.2	82.0
ethylene [a]	1	–	–
propylene	2	33.7	87.0
nitrogen [a]	1	–	–
carbon dioxide	1	49.8	652.5
hydrogen sulfide	1	85.1	84.9

[a] No upper quadruple point for this gas

[b] Structure formed depends on temperature.

Table 9B2.4 – Kihara Parameters for Calculating Langmuir Constants

Gas	2a (ångstroms)	σ (ångstroms)	ε/k (°R)
methane	0.7668	3.1710	278.17
ethane	1.1302	3.2541	318.44
propane	1.3004	3.3074	376.13
isobutane	1.6000	3.1244	396.94
cyclopropane	1.0000	3.4559	379.04
ethylene	0.9400	3.2910	311.17
propylene	1.3000	3.2304	364.36
nitrogen	0.7052	2.8950	244.82
carbon dioxide	1.3610	2.9718	302.89
hydrogen sulfide	0.7200	3.1989	365.40

Table 9B2.5 – Constants for Calculating Dissociation Pressures of Reference Hydrates

	A_R	B_R	C_R	Temperature Range °F
Structure I	24.1313	–6,043.63	–1.8500	–80 to 32
	–1,322.5387	79,819.2	187.719	32 to 80
Structure II	11.3257	–7,366.27	0.316033	–4 to 32
	–1,117.1406	62,971.7	159.923	32 to 64
	4,424.168	–348,171.8	–599.755	64 to 86

Note: For pressures measured in atm and temperatures measured in °R.

Table 9B2.6 – Thermodynamic Properties of Empty Hydrate (β Phase) and Liquid Water Relative to Ice (α Phase) at 0 °C and No Pressure

	Structure I	Structure II
$\mu_w^{\beta}-\mu_w^{\alpha}$, Btu/lb-mole	543.6	379.8
$h_w^{\beta}-h_w^{\alpha}$, Btu/lb-mole	495.0	347.4
$v_w^{\beta}-v_w^{\alpha}$, ft^3/lb-mole	4.8056×10^{-2}	5.4463×10–2
$h_w^{L}-h_w^{\alpha}$, Btu/lb-mole	2592.0	
$C_p^{L}-C_p^{\beta}$, Btu/lb-mole (T in °R)	9.11 – 0.01867 (T – 491.7)	

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