STANDARD OPERATING PROCEDURE

SAMPLE PREPARATION AND CALCULATIONS FOR DISSOLVED GAS ANALYSIS IN WATER SAMPLES USING A GC HEADSPACE EQUILIBRATION TECHNIQUE

DISCLAIMER:

This standard operating procedure has been prepared for the use of the R.S. Kerr Environmental Research Laboratory of the United States Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

1. **Purpose: (Scope and Application)**

This method is applicable to the preparation of water samples for analysis of the headspace to quantify part-per-million levels of dissolved gases in the water sample. Although this method is specifically for determining methane, ethene, ethane, and nitrous oxide, it has also been used to determine vinyl chloride, nitrogen, oxygen and carbon dioxide in both laboratory and field samples. The number of analyses that can be performed in one eight hour day is approximately 30.

This method is restricted to use by or under the supervision of analysts experienced in sample preparation and in the use of gas chromatography and the interpretation of chromatograms.

2. **Summary of Method:**

A water sample is collected, in the field or in the laboratory, in a serum bottle and capped using a Teflon faced septum and crimp cap of the appropriate size to fit the bottle. A headspace is prepared using high purity helium. The bottle is shaken for 5 minutes and a sample is taken of the headspace and injected onto a gas chromatographic column where the gaseous components are separated and detected by flame ionization detector or electron capture detector. By using Henry's law, the concentration of the gas in the headspace, the bottle volume, and temperature of the sample, the concentration of dissolved gas in the original water sample can be determined.

3. **References:**

3.1 Kampbell, D. H.,J. T. Wilson, S. A. Vandegrift, Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique, International Journal of Environmental Analytical Chemistry, Volume 36, pp. 249-257,1991.

3.2 Vandegrift, S.A., RSKSOP-114, Revision Number 0, January 1991.

3.3 Newell, B.S., RSKSOP-147, Revision Number 0, August 1993.

3.4 Perry, J.H., *Chemical Engineer's Handbook*, (McGraw-Hill, New York, 1978), 5th ed.

4. **Procedure:**

Sample Collection and Preparation:

Water samples should be collected in the field or prepared in the lab by placing the water in a glass bottle. Typically, a 60 milliliter serum bottle is used. Add the water down the side of the bottle so as not to agitate or contaminate the sample. Fill to the top and cap using a butyl rubber Teflon faced septum and the appropriate size aluminum crimp cap. Care should be taken so there are no bubbles in the bottle. Field samples should be fixed with 1:1 hydrochloric acid to a pH less than 2 before they are capped. Do not add acid if carbon dioxide analysis is to be performed since it may convert inorganic carbon to carbon dioxide. Store samples at 4 C and analyze within 14 days of collection.

Remove samples from the refrigerator and allow them to come to room temperature. To generate headspace in the sample bottle, place the bottle upside down in a three finger clamp attached to a ring stand. Next, insert through the septum a 20 gauge needle attached to a 10 ml Luerlock glass syringe set for dead volume. Then insert an 8 cm 20 gauge needle attached to Teflon tubing with a needle valve is inserted through the septum to the bottom of the bottle. The Teflon tubing is attached to a two-stage regulator on a cylinder of high purity helium and the helium is passed through the needle at 5 ml per minute or less.

NOTE: Helium should be allowed to flow through the Teflon tubing and needle for 30 minutes prior to preparation of the first sample, and flow should continue throughout the day.

The helium forces water out of the bottle and into the glass syringe. The amount of water taken out of the bottle should be 10% of the volume of the sample bottle up to the 100 ml size. If a 160 ml serum bottle is used, remove only 10 ml of the water during sample preparation. After the appropriate amount of water has been removed, pull the 8 cm needle out of the septum. Next, pull the syringe from the septum. The sample bottle is then shaken at 1400 rpm on a rotary shaker for 5 minutes to allow the gases to equilibrate between the headspace and the liquid phase. A portion of the headspace is then taken immediately for analysis on the gas chromatograph. Use a 500 microliter gas tight syringe to take a 300 microliter sample of the headspace. This is done by inserting the syringe needle into the septum so that the side port of the needle is in the headspace. Pull the plunger up to the 300 microliter mark. Close the syringe and withdraw the needle from the septum. Inject the syringe's contents into a gas chromatograph for analysis.

The GC conditions for the analysis of methane, ethane, ethene, and nitrous oxide can be found in RSKSOP-147; for carbon dioxide, oxygen, and nitrogen the conditions for the GC are found in RSKSOP-114. After GC analysis is successfully completed, remove the cap from the bottle.

CAUTION: Excessive handling of the sample should be avoided, as this will raise the temperature of the sample.

Record the temperature of the remaining sample using a thermometer, then record the volume of the sample bottle by refilling the bottle and pouring its contents into a Class "A" calibrated to contain (TC) graduated cylinder. Along with the samples a method blank should also be analyzed. The method blank consists of deionized water prepared in the same type of bottle used for the samples. Area count for any detected analyte is subtracted from the area count for each sample. See example calculations.

5. Calculations:

5a. General Equations:

The calculations for dis ived gas concentration involve several steps. In this section the general steps and equations will be given; in section 5b a specific exa le for methane will be shown. Parameters needed are partial pressure of the a lyte(p_g)(the analyte is the gas in question), Henry's law constant (H), tempera ure of the sample, volume of the sample bottle, and molecular weight of the a lyte.

1) From the analysis of th sample, an area count is obtained. Using this area count and the regression e ation of the standard curve, the partial pressure is determined.

NOTE: To determine the re ssion equation, plot area count versus concentration of the standard gas in th decimal fraction i.e. 10 ppm would be 0.00001 on the curve.

NOTE: In these calcula ons total pressure is assumed to be equal to 1 atmosphere; therefore, p_g . = p_g.

p_g = m(sample area ount) + b Eqn. 1
where p_g = partial essure of the gas (decimal fraction)
m = slope of the ne of the standard curve
b = y-intercept o the line.

2) The equilibrium mole f ction of the dissolved gas, $x_g = p_g/H$ Eqn. 2
where H = Henry's l constant for the gas.

3) Let n_g = moles analyte nd n_w = moles water.
Then $x_g = n_g/(n_g + n_w)$ and = $x_g(n_g + n_w)$. Eqn. 3
if $n_g \cdot x_g << n_g$,
then $n_g = x_g \cdot n_w$ or = $n_w(p_g/H)$
therefore, $n_g/V = n$ (p_g/H) Eqn.4.

4) One liter of water i 5.5 g-moles,
n_g/V= 55.5 moles/L(H)

5) Saturation concentrati of the gas,
$C = (n_g/V)(MW)(1000$ g/g) Eqn. 5
where MW = mo cular weight of the analyte.

6) Density calculation
p = (molecular wei of the analyte)/(22.4 l/mole)(ST in K/273° K)
where p = de ty
ST = sa e temperature

7) $v = bv_{mls} - hv_{mls}$(1L/10 ls) Eqn. 7
where bv = b tle volume
hv = h dspace volume

Then,

8) $A_h = hv_{mls} * p_g$
where A_h = ml of a lyte in headspace
then liquid phase anal (A_l) is

$A_1 = (A_h/(v))(p)(1000mg/g)(1l/1000ml)$ Eqn. 8.

Then $TC = A_1 + C$

where TC = Total Concentration of analyte in the original sample
A_1 = liquid phase analyte from Eqn. 8
C = saturation conc. from Eqn. 5.

The result will be in units of milligrams of gas per liter of water.

5b. Example Calculation

Methane will be used as the example of the calculation for dissolved gas concentration in water. From the analysis of the sample, an area count for methane is determined. This area count is used with the equation for the line of the standard curve, which is determined by analyzing a range (10 - 10,000 ppm CH_4) of methane standards, to obtain the partial pressure.

Parameters for this example calculation are as follows:
sample area count = 978264
method blank area count = 2766
Henry's law constant = 4.13E+4 (at 25 C)
sample temperature = 25 C
bottle volume = 60 ml
headspace volume = 6 ml.

1) For this sample the equation for the line of the standard curve is
$pg = 1.814E-9x - 6.716E-6$
$\therefore p_g = (1.814E-9(978264-2766)) - 6.716E-6$ Eqn. 1
so, $p_g = 0.0018$.

2) Using Eqn. 2, $x_g = 0.0018 / 4.13E+4$ or 4.269E-8 mole CH_4.

3 & 4) Using Eqn. 4 and the value above, $n_g/V = (55.5)(4.269E-8)$
or 2.37E-6 moles CH_4 / liter H_2O

5) Saturation concentration of CH_4, using Eqn. 5 and the value for n_g/V
$C = (2.37E-6)(16)(1000) = 0.038$ mg CH_4 / liter H_2O.

6) $p = (16g/mole)/((22.4liters/mole)(298/273)) = 0.654$ g CH_4 / liter.

7) bv = 60 ml and hv = 6 ml,
$v = (60 ml - 6 ml)(1L/1000ml) = 0.054$ L.

8) $A_h = 6ml \cdot 0.0018 = 0.0108$ ml CH_4
$A_l = (0.0108 ml / 0.054 l)(0.654 g/l)(1l/1000ml)(1000mg/g)$
$A_l = 0.1308$ mg CH_4 / l H_2O

9) then $TC = A_l + C = 0.038mg/l + 0.131mg/l$
$TC = 0.169$ mg CH_4/liter H_2O.

6. Quality Control:

The use of method blanks, field blanks, field replicates and laboratory duplicates are encouraged. See the SOPs used for the GC analysis for information on analytical quality control.

PRECAUTIONS: No special precautions are necessary aside from those used in good laboratory practice.

NOTE: See appendix for tables of Henry's law constants.

GAS ABSORPTION

References: Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952. Leva, "Tower Packings and Packed Tower Design," U.S. Stoneware Co., Akron, Ohio, 1953. Treybal, "Mass-transfer Operations," McGraw-Hill, New York, 1955. Morris and Jackson, "Absorption Towers," Butterworth, London, 1953. Brown, "Unit Operations," Wiley, New York, 1950. Cremer and Davies, "Chemical Engineering Practice," vol. 6, Academic Press, New York, 1956. Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering," 3d ed., McGraw-Hill, New York, 1937. McCabe and Smith, "Unit Operations of Chemical Engineering," McGraw-Hill, New York, 1956. Colburn, *Trans. Am. Inst. Chem. Engrs.*, **35**, 211 (1939). Colburn, *Ind. Eng. Chem.*, **33**, 459 (1941). Unit Operations Reviews, *Ind. Eng. Chem.*, **42**, 17 (1950); **34**, 41 (1951); **44**, 25 (1952); **45**, 957 (1953); **46**, 61, 937 (1954); **47**, 505, 658 (1955); **48**, 468, 669 (1956); **49**, 457, 577 (1957); **50**, 421, 856 (1958); **51**, 237, 464 (1959). Kohl and Riesenfeld, *Chem. Eng.*, **66** (12), 127 (1959).

INTRODUCTION

Gas absorption is a unit operation in which a soluble component of a gas mixture is dissolved in a liquid. The inverse operation, called **stripping** or **desorption**, is employed when it is desired to transfer a volatile component from a liquid mixture into a gas. The following section is concerned principally with the design of commercial equipment for carrying out either of these operations continuously. Many gaseous materials are amenable to gas-absorption processes. Table 14-1 lists some gas-absorption systems of commercial importance.

The apparatus used for contacting a liquid and a gas stream continuously may be a tower filled with irregular solid packing material, an empty tower into which the liquid is sprayed, or a tower containing a number of bubble-cap or sieve plates. Ordinarily, the gas and liquid streams flow countercurrently through the equipment in order to obtain the greatest rate of absorption. Occasionally, gas-absorption operations are carried out in spray columns, wetted-wall columns, stirred vessels, or mechanically aided devices.

There are three main steps in design of an absorption or stripping tower:

1. Data on the vapor-liquid equilibrium relations for the system are used to determine (*a*) the quantity of liquid needed to absorb the required amount of the soluble component from the gas or (*b*) the quantity of gas needed to strip the required amount of the volatile component from the liquid.
2. Data on the liquid- and vapor-handling capacity of equipment of the type being considered are used to determine the required cross-sectional area of the channels through which the liquid and vapor streams will flow. (Economic factors may dictate use of fluid velocities well below the maximum values that can be employed.)
3. Equilibrium data and material balances are used to determine the number of equilibrium stages (theoretical plates or transfer units) required for the separation desired. Difficulty of the separation depends on the degree of recovery that is economically most desirable. Required time of contact between the flowing streams, or required height of the tower, can be calculated if data are available for the specific rate of transfer of material between the gas and liquid phases, expressed in terms of the plate efficiency or the height of one transfer unit (H.T.U.).

EQUILIBRIUM DATA

Solubility of Various Gases in Water. In order to define the solubility factor of a gas in a liquid, it is generally necessary to state the temperature, the equilibrium partial pressure of the solute gas in the gas phase, and the concentration of the solute gas in the liquid phase.

Table 14-1. Gas-absorption Systems of Commercial Importance*

Solute	Solvent	Reagent	Degree of commercial importance: High	Moderate	Low
SO_2, H_2S	Water	.....	x		
SO_2, H_2S	Water	Monoethanolamine	x		
SO_2, H_2S	Water	Diethanolamine	x		
SO_2, H_2S	Water	Triethanolamine			
SO_2, H_2S	Water	Diisopropanolamine	...	...	x
SO_2, H_2S	Water	Methyl diethanolamine	...	...	x
SO_2, H_2S	Water	K_2CO_3, $NaCO_3$	...	...	x
SO_2, H_2S	Water	NH_3	x		
SO_2, H_2S	Water	NaOH, KOH	...	x	
SO_2, H_2S	Water	K_3PO_4	...	x	
SO_2	Propylene carbonate	.....	...	x	
SO_2	Glycerol triacetate	.....	...	x	
SO_2	Butoxy diethylene glycol acetate	.....	...	x	
SO_2	Methoxy triethylene glycol acetate	.....	...	x	
HCl, HF	Water	.....	...	x	
HCl, HF	Water	NaOH	x		
Cl_2	Water	.....	x		
SO_2	Water	.....			
SO_2	Water	NH_3	...	x	
SO_2	Water	Xylidine	...	x	
SO_2	Water	Dimethyl aniline	...	x	
SO_2	Water	$Ca(OH)_2$, oxygen	...	...	x
SO_2	Water	Aluminum hydroxide-sulfate	...	x	
NH_3	Water	.....	x		
NO_x	Water	.....	x		
HCN	Water	NaOH	x		
CO	Water	Copper ammonium salts	x		

* Kohl and Riesenfeld, *Chem. Eng.*, **66** (12), 127 (1959); Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.

PERRY'S CHEMICAL ENGINEERS' HANDBOOK. 1963. J.H. Perry (ed). McGRAW-HILL, NEW YORK, NY 4TH ed.

(Strictly speaking the total pressure on the system as well as the partial pressure of the solute gas should be stated, but where the total pressure is not more than a few, perhaps 5, atmospheres, the solubility for a particular partial pressure of solute gas may be safely considered independent of total pressure.) The solubility of NH_3 (Table 14-4) at a temperature of 30°C. for a partial pressure of NH_3 of 260 mm. is given as 20 weights of NH_3 per 100 weights of H_2O. This method of stating temperature, partial pressure of solute gas in the gas phase, and concentration of solute in the liquid phase will be employed for systems where Henry's law does not hold.

If Henry's law holds, solubility is defined by giving the Henry's law constant H and the temperature where $H = p_A/x_A$ = atm./mole fraction of solute in solution. For quite a number of gases, Henry's law holds very well where the partial pressure of the solute gas does not exceed 1 atm. For partial pressures of solute gas greater than 1 atm., H is seldom independent of the partial pressure of the solute gas, and a given value of H can be used over only a narrow range of partial pressures. In defining gas solubility at these higher pressures, the partial pressure of the solute gas as well as the temperature and the value of H must be specified. In the following tables, if the partial pressure of the solute gas is not specified, the values of H may be safely used only for partial pressures of solute gas not greater than 1 atm. Where the partial pressure of the solute gas is specified, the given values of H may be used for partial pressures not more than perhaps an atmosphere higher or lower than the stated partial pressure. The use of Henry's law constants is illustrated by the examples given below.

Example 1. It is desired to find out how much hydrogen can be dissolved in 100 weights of water from a gas mixture when the total pressure is 760 mm. Hg, the partial pressure of H_2 is 200 mm., and the temperature is 20°C.

For partial pressures of H_2 up to 1 atm., the value of H is 6.83×10^4 at 20°C. (see Table 14-19).

$$x_A = \frac{p_A}{H} \qquad (14\text{-}1)$$

$$p_A = \frac{200}{760} = 0.263 \text{ atm.}$$

$$x_A = \frac{0.263}{68,300} = 0.00000385$$

where x_A is the mole fraction of H_2 in the liquid phase. (Mole fraction is the ratio of the number of moles of a particular constituent contained in a given weight of the solution to the total moles of all constituents contained.) To calculate the units of weight of H_2 per 100 weights of H_2O, the following formula may be used:

$$\left(\frac{x_A}{1 - x_A}\right)\frac{M_A}{M_B}100 = \left(\frac{0.00000385}{1 - 0.00000385}\right)\frac{2.02}{18.02}100 = 0.0000431$$

Thus, 0.0000431 weight of H_2 may be dissolved in 100 weights of H_2O at 20°C. from a gas mixture where the partial pressure of H_2 is 200 mm.

Example 2. Oxygen is dissolved in water to the extent of 0.03 weight of O_2 per 100 weights of H_2O. What equilibrium partial pressure of O_2 would this solution exert at 25°C.?

Take as a basis 100 weights of H_2O.

$$x_A = \frac{0.03/32}{0.03/32 + 100/18} = 0.0001688$$
$$p_A = Hx_A$$

If p_A is greater than 1 atm., the value of p_A should be known before the proper value of H can be selected. A trial-and-error solution is indicated. As a first approximation, assume the p_A will not exceed 1 atm. and select the value of H corresponding to 25°C. from Table 14-27.

$$H = 4.38 \times 10^4$$
$$p_A = 43,500 \times 0.0001688 = 7.39 \text{ atm.}$$

Select another value of H for a partial pressure of 7.39 atm. (5620 mm.) from Table 14-28, interpolating to obtain a value for 25°C.

$$H = 4.89 \times 10^4$$
$$p_A = 48,900 \times 0.0001688 = 8.25 \text{ atm.} = 6280 \text{ mm.}$$

A third approximation, using Table 14-28, assuming $p_A = 8.25$ atm., gives a value of p_A which is as accurate as the available values of H will permit.

$$H = 4.86 \times 10^4$$
$$p_A = 49,200 \times 0.0001688 = 8.35 \text{ atm.} = 6350 \text{ mm.}$$

Thus, 0.03 weight of O_2 dissolved in 100 weights of H_2O would exert a partial pressure of 6350 mm. at 25°C.

There may also be a sufficiently close, though less accurate, proportionality between the concentrations of the gas in the liquid and the gas phases when compositions are expressed in other units, particularly when comparatively dilute solutions are involved. Henry's law, though quite useful if it can be applied, must be checked experimentally in each instance to determine the accuracy with which it can be used. The following tables and charts give data on the solubility of some of the more common gases in water.

The solubility tables have been taken from the "International Critical Tables" and other reliable sources. In many instances, the tables here presented represent only a part of the solubility data given in the original. Where the data given are not sufficient for a particular problem, reference to the original is recommended. Markham and Kobe [*Chem. Rev.*, **28**, 519 (1941)] have summarized and critically reviewed the gas-solubility data that were available prior to 1941. Reference may also be made to Seidell and Linke, "Solubilities of Inorganic and Metal Compounds," Van Nostrand, Princeton, N.J., 1952.

Table 14-8.[1] Acetylene (C_2H_2)

t, °C	0	5	10	15	20	25	30
$10^{-4} \times H$*	0.72	0.84	0.96	1.08	1.21	1.33	1.46

[1] "International Critical Tables," vol. 3, p. 260, McGraw-Hill, 1928.

[1] Superior numbers refer to table footnote references on p. 14-7.

* The H in these solubility tables is the proportionality constant for the expression of Henry's law, $p = Hx$, where x = mole fraction of the solute in the liquid phase; p = partial pressure of the solute in the gas phase, expressed in atmospheres; H = a proportionality constant and is in units of atmospheres of solute pressure in the gas phase per unit concentration of the solute in the liquid phase. (The unit of concentration of the solute in the liquid phase is moles solute per mole solution.)

Table 14-9.[2] Air

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$*	4.33	4.88	5.49	6.07	6.64	7.20	7.71	8.25

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$*	8.70	9.11	9.46	10.1	10.5	10.7	10.8	10.7

[2] "International Critical Tables," vol. 3, p. 257.

* H is calculated from the absorption coefficients of O_2 and N_2, taking into consideration the correction for constant argon content.

According to Whitney and Vivian [*Ind. Eng. Chem.*, **33**, 741 (1941)], the solubility of chlorine in water, in lb.-moles Cl_2/cu. ft., follows the equation

$$C = H'p + (K_e H'p)^{1/2} \qquad (14\text{-}2)$$

obtained by assuming that the solubility of molecular chlorine follows Henry's law and that the equilibrium in the hydration reaction

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$

is represented by an equilibrium constant K_e. The observed values of H' and K_e are given in Table 14-12.

Solubility of Gases in Non-aqueous Pure Liquids. The solubility of a gas in a non-aqueous pure liquid is

Table 14-4.[3,4] Ammonia (NH_3)

Weight NH_3 per 100 weights H_2O	Partial pressure of NH_3, mm. Hg							
	0°C.	10°C.	20°C.	25°C.	30°C.	40°C.	50°C.	60°C.
100	640							
90	705							
80	636	987	1490	.....	.....	3000		
70	500	780	1170	.....	.....	2360		
60	380	600	945	.....	.....	2130		
50	275	439	686	.....	.....	1520		
40	190	301	470	.....	710	1065		
30	119	190	298	.....	454	692		
25	89.5	144	227	.....	352	584	825	
20	64	103.5	166	.....	260	395	586	834
15	42.7	70.1	114	.....	179	273	405	565
10	25.1	41.8	69.6	.....	110	167	247	351
7.5	17.7	29.9	50.0	.....	79.7	120	176	251
5	11.2	19.1	31.7	.....	51.0	76.5	115	165
4	.....	14.1	24.9	.....	40.1	60.8	91.1	129.2
3	.....	11.3	18.2	23.5	29.6	45	67.1	94.3
2.5	.....	.....	15.0	19.4	24.4	(32.6)*	(45.7)*	72.0
2	.....	.....	12.0	15.3	19.3	(26.0)	(44.5)	61.0
1.6	.....	.....	.....	12.0	15.3	(24.1)	(35.5)	48.7
1.2	.....	.....	.....	9.1	11.5	(18.5)	(26.7)	36.5
1.0	.....	.....	.....	7.4	.....	(15.4)	(22.2)	30.2
0.5	.....	.....	.....	3.4				

* Extrapolated values.

Table 14-5. Ammonia (NH_3)

Weight NH_3 per 100 weights H_2O	0.105	0.244	0.52	0.38	0.576	0.751	1.02
Partial pressure NH_3, mm. Hg, at 25°C.	0.791	1.83	2.41	2.89	4.41	5.80	7.96
Weight NH_3 per 100 weights H_2O	1.31	1.53	1.71	1.98	2.11	2.56	2.75
Partial pressure NH_3, mm. Hg, at 25°C.	10.31	11.91	13.46	15.75	16.94	20.86	22.38

"Landolt-Börnstein Physikalisch-chemische Tabellen," Eg. I, p. 303, 1927. Phase-equilibrium data for the binary system NH_3-H_2O are given by Clifford and Hunter, *J. Phys. Chem.*, **37**, 101 (1933).

Table 14-6.[3,4] Bromine (Br_2)

t, °C	0	5	10	15	20	25
$10^{-3} \times H$	0.215	0.275	0.366	0.466	0.595	0.757

t, °C	30	40	50	60	70	80
$10^{-3} \times H$	0.905	1.93	1.91	2.51	3.21	4.04

"International Critical Tables," vol. 3, p. 255.

Table 14-7.[3,4] Carbon Dioxide (CO_2)

t, °C	0	5	10	15	20	25	30	35	40	45	50	60
$10^{-3} \times H$	0.728	0.876	1.04	1.22	1.42	1.64	1.86	2.09	2.33	2.57	2.83	3.41

"International Critical Tables," vol. 3, p. 260.

Table 14-8.[21] Carbon Dioxide (CO_2)

Total pressure, atm.	Weight of CO_2 per 100 weights of H_2O*								
	17°C.	18°C.	25°C.	31.04°C.	35°C.	40°C.	50°C.	75°C.	100°C.
25	.....	3.56	.....	3.60	2.56	2.30	1.92	1.35	1.05
50	7.03	6.33	5.38	4.77	4.39	4.02	3.41	2.49	2.01
75	7.18	6.69	6.17	5.60	5.31	5.10	4.45	3.32	2.82
100	7.27	6.72	6.28	5.97	5.76	5.50	5.07	4.09	3.49
150	7.39	7.07	.....	6.25	6.03	5.81	5.47	4.86	4.49
200	.....	.....	.....	6.48	6.29	6.28	5.76	5.27	5.08
300	7.66	7.35	.....	.....	.....	.....	6.20	5.83	5.84
400	8.12	7.77	7.54	7.27	7.06	6.89	6.56	6.36	6.40
500	.....	.....	.....	7.65	7.51	7.36	.....	.....	.....
700	.....	.....	.....	.....	.....	.....	7.38	7.43	7.61

* In the original, concentration is expressed in cubic centimeters of CO_2 (reduced to 0°C. and 1 atm.) dissolved in 1 g. of water.

frequently of great interest to the chemical engineer. The possible combinations of solutes and solvents that come under the above classification are very numerous. Solubility tables in the "International Critical Tables," "Landolt-Börnstein Physikalisch-chemische Tabellen," and Seidell and Linke ("Solubilities of Inorganic and Organic Compounds," Van Nostrand, Princeton, N.J., 1952) present most of the available data. The list of solutes and solvent in Table 14-34 will give some idea of the type of systems for which solubility data are available. The list, which has been made up from tables appearing in the "International Critical Tables," vol. 3, pp. 261–270, does not include, by any means, all the solutes and solvents considered in the "International Critical Tables," but only some of those most commonly encountered.

Solubility data for hydrocarbons in oil are usually expressed in the form of an equilibrium constant $K = y^*/x$, where y^* = mole fraction of the solute in the gas phase, and x = mole fraction of the solute in the liquid phase. The value of K varies with temperature, pressure, and composition (see p. 13-13). Values of K are given by Katz and Hachmuth [*Ind. Eng. Chem.*, **29, 1072 (1937)]. See also Sherwood and Pigford ("Absorption and Extraction," McGraw-Hill, New York, 1952) and an extensive series of articles by Sage *et al.* [*Ind. Eng. Chem.*, 1934 to date]. The available data are discussed in Sec. 13.**

Solubilities of Gases in Aqueous Solutions. These data may be found in Seidell, Landolt-Börnstein, and the "International Critical Tables," vol. 3, pp. 271–281. The solutes considered in the "International Critical Tables" include, in general, the same gases as listed in Table 14-34. The solvents are aqueous solutions containing various concentrations of both inorganic and

Table 14-9.[3,4] Carbon Monoxide (CO)

t, °C	0	5	10	15	20	25	30	35
$10^{-3} \times H$	3.53	3.96	4.42	4.89	5.36	5.80	6.20	6.59

t, °C	40	45	50	60	70	80	90	100
$10^{-3} \times H$	6.96	7.29	7.61	8.21	8.45	8.45	8.46	8.46

"International Critical Tables," vol. 3, p. 260.

Table 14-10.[3] Carbon Monoxide (CO)

Partial pressure of CO, mm. Hg	$10^{-3} \times H$	
	17.5°C.	99.0°C.
1000	4.77	4.86
2000	4.77	4.91
3000	4.77	4.95
4000	4.78	4.95
5000	4.80	4.97
6000	4.82	4.98
7000	4.84	5.02
8000	4.86	5.08

"International Critical Tables," vol. 3, p. 260.

Table 14-11. Carbonyl Sulfide (COS)

t, °C	0	5	10	15	20	25	30
$10^{-3} \times H$	0.92	1.17	1.46	1.82	2.19	2.59	3.04

"International Critical Tables," vol. 3, p. 261.

Table 14-12. Chlorine (Cl_2)

Temp., °C.	Henry's law coefficient H', lb.-moles Cl₂/cu. ft./atm.	Equilibrium constant K_e, (lb.-moles/cu. ft.)[2]
10	0.00707	7.10
15	.00584	8.55
20	.00489	10.2
25	.00410	12.8

Whitney and Vivian, *Ind. Eng. Chem.*, **33**, 741 (1941).

Table 14-13.[28] Chlorine (Cl_2)

Partial pressure of Cl_2, mm. Hg	Solubility, g. of Cl_2 per liter					
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.
5	0.468	0.451	0.436	0.424	0.412	0.398
10	.929	.893	.875	.853	.832	.812
20	1.821	1.624	.937	.873	.821	.761
30	1.717	1.554	1.349	1.196	1.033	.962
100	2.79	2.66	1.775	1.595	1.434	1.313
150	3.81	2.73	2.72	1.966	1.754	1.599
200	4.78	3.55	2.74	2.34	2.05	1.856
250	5.71	5.05	3.16	2.69	2.34	2.09
300	.....	4.54	3.63	3.08	2.61	2.31
350	.....	5.13	4.06	3.35	2.86	2.53
400	.....	5.71	4.48	3.69	3.11	2.74
450	.....	6.26	4.88	3.98	3.36	2.94
500	.....	6.85	5.29	4.30	3.61	3.14
550	.....	7.39	5.71	4.65	3.84	3.33
600	.....	7.97	6.12	4.91	4.08	3.52
650	.....	8.52	6.52	5.21	4.32	3.71
700	.....	9.09	6.90	5.50	4.54	3.89
750	.....	9.65	7.29	5.80	4.77	4.07
800	.....	10.21	7.69	6.08	4.99	4.27
900	.....	.....	8.46	6.68	5.44	4.62
1000	.....	.....	9.22	7.22	5.88	4.97
1200	$Cl_2.8H_2O$ separates		10.84	8.42	6.81	5.62
1500	.....	.....	13.23	10.14	8.05	6.78
2000	.....	.....	17.07	13.02	10.22	8.58
2500	.....	.....	21.0	15.84	12.32	10.05
3000	.....	.....	.....	18.73	14.47	11.70
3500	.....	.....	.....	21.7	16.62	13.38
4000	.....	.....	.....	24.7	18.84	15.04
4500	.....	.....	.....	27.7	20.7	16.75
5000	.....	.....	.....	30.8	23.3	18.46

Partial pressure of Cl_2, mm. Hg	Solubility, g. of Cl_2 per liter					
	60°C.	70°C.	80°C.	90°C.	100°C.	110°C.
5	0.383	0.369	0.351	0.339	0.326	0.316
10	.492	.470	.447	.431	.415	.402
20	.745	.704	.671	.642	.627	.598
30	.912	.863	.815	.781	.747	.722
100	1.228	1.149	1.085	1.034	.987	.950
150	1.482	1.352	1.294	1.227	1.174	1.137
200	1.706	1.580	1.479	1.396	1.333	1.276
250	1.914	1.764	1.642	1.553	1.480	1.413
300	2.10	1.932	1.793	1.700	1.610	1.542
350	2.28	2.10	1.940	1.831	1.736	1.661
400	2.47	2.25	2.08	1.965	1.854	1.773
450	2.64	2.41	2.22	2.09	1.972	1.880
500	2.80	2.55	2.35	2.21	2.08	1.986
550	2.97	2.69	2.47	2.32	2.19	2.09
600	3.13	2.83	2.59	2.43	2.29	2.19
650	3.29	2.97	2.72	2.55	2.41	2.28
700	3.44	3.10	2.84	2.66	2.50	2.37
750	3.59	3.23	2.96	2.76	2.60	2.47
800	3.73	3.37	3.08	2.87	2.69	2.56
900	4.04	3.63	3.30	3.08	2.89	2.74
1000	4.36	3.88	3.53	3.28	3.07	2.91
1100	4.92	4.37	3.95	3.67	3.43	3.25
1500	5.76	5.09	4.58	4.23	3.95	3.74
2000	7.14	6.26	5.63	5.17	4.78	4.49
2500	8.48	7.40	6.61	6.05	5.59	5.25
3000	9.83	8.52	7.54	6.92	6.38	5.97
3500	11.22	9.65	8.53	7.79	7.16	6.72
4000	12.54	10.76	9.52	8.65	7.94	7.42
4500	13.88	11.91	10.46	9.49	8.72	8.13
5000	15.26	13.01	11.42	10.35	9.48	8.84

organic compounds. Among the inorganic compounds are included many common acids, bases, and salts. Some of the organic compounds considered are: methyl alcohol, ethyl alcohol, glycerol, glucose, sucrose, chloral hydrate, and urea.

Solubilities of gases, particularly carbon dioxide, hydrogen, and nitrous oxide, in certain colloidal solutions in water may be found in the "International Critical Tables," vol. 3, p. 251. Typical colloids considered are gelatin, starch, dextrin, egg albumen, serum albumen, glycogen, peptone, hemoglobin, arsenic trisulfide, ferric hydroxide, and silicic acid.

Data on solubility under pressures up to 200 atm. for N_2, H_2, O_2, CH_4, C_6H_6, C_2H_6, C_3H_8, and H_2S in water and a number of organic solvents are given by Frolich, Tauch, Hogan, and Peer [*Ind. Eng. Chem.*, **23**, 548 (1931)]. Goodman and Krase [*Ind. Eng. Chem.*, **23**, 401 (1931)] present experimental data on the solubility of N_2 in water at pressures from 100 to 300 atm. and temperatures from 0° to 170°C. Wiebe and Gaddy [*J. Am. Chem. Soc.*, **61**, 315 (1939)] give data up to 700 atm. and from 50° to 100°C.

Ether Vapor in Various Solvents. The recovery of ether vapor is frequently accomplished by absorption in a liquid absorbent such as sulfuric acid or meta-cresol.

Table 14-14. Chlorine Dioxide (ClO_2)

Vol. % of ClO_2 in gas phase	Weight of ClO_2, grams per liter of solution						
	0°C.	5°C.	10°C.	15°C.	20°C.	30°C.	40°C.
1	2.80	1.7	1.25	1.00	0.90	0.60	0.44
2	4.80	[illegible]	2.65	2.28	2.20	1.95	1.30
3	10.0	[illegible]	4.30	3.25	4.30	3.20	2.25
5	14.0	[illegible]	8.95	7.35	6.15	4.40	3.20
10	20.0	15.5	12.8	10.5	8.80	6.30	4.50
11	.....	17.0	14.0	11.7	9.70	7.00	5.00
12	.....	18.6	15.3	12.8	10.55	7.50	5.45
13	.....	20.3	16.6	13.8	11.5	8.20	5.85
14	.....	.....	18.0	14.9	12.5	8.80	6.35
15	.....	.....	19.2	16.0	13.2	9.50	6.80
16	.....	.....	20.3	17.0	14.2	10.1	7.20

Ishi, *Chem. Eng. (Japan)*, **22**, 153 (1958).

Table 14-15.[3] Ethane (C_2H_6)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	1.26	1.55	1.89	2.26	2.65	3.02	3.42	3.83

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	4.25	4.63	5.00	5.65	6.23	6.61	6.87	6.92

"International Critical Tables," vol. 3 p. 261.

Table 14-16.[3] Ethylene (C_2H_4)

t, °C	0	5	10	15	20	25	30
$10^{-4} \times H$	5.52	6.55	7.60	8.95	10.2	11.4	12.7

"International Critical Tables," vol. 3, p. 260.

Table 14-17. Helium (He)

t, °C	0	10	20	30	40	50
$10^{-4} \times H$	12.9	12.6	12.5	12.4	12.1	11.5

See also Pray, Schweickert, and Minnich, *Ind. Eng. Chem.*, **44**, 1146 (1952).

Table 14-18.[9,22,23] Hydrogen (H_2)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	5.39	6.08	6.56	6.61	6.83	7.07	7.29	7.42

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	7.51	7.60	7.65	7.65	7.61	7.55	7.51	7.45

"International Critical Tables," vol. 3, p. 256.
See also Pray, Schweickert, and Minnich, *Ind. Eng. Chem.*, **44**, 1146 (1952).

Table 14-19.[10] Hydrogen (H_2)

Partial pressure H_2, mm. Hg	$10^{-4} \times H$	
	19.5°C.	25°C.
900	7.[illegible]	
1100	.....	7.35
2000	7.42	7.36
3000	7.45	7.77
4000	7.47	7.81
5000	7.56	7.89
6000	7.70	8.00
7000	7.87	8.16
8200	.....	8.41
8250	8.17	

"International Critical Tables," vol. 3, p. 256.

Table 14-20.[14] Hydrogen Chloride (HCl)

Weights of HCl per 100 weights of H_2O	Partial pressure of HCl, mm. Hg			
	0°C.	10°C.	20°C.	30°C.
76.6	310	440		
66.7	130	233		
58.3	39.8	56.4	388	627
50.8	5.7	11.8	82.5	188
44.5	1.0	2.27	25.5	44.5
39.4	0.175	0.48	4.98	9.98
35.0	.0316	.084	1.088	2.17
31.6	.0056	.016	0.295	0.48
29.05	.00099	.0029	.0428	.086
27.04	.000318	.000905	.0088	.0244
25.38	.000118	.000383	.00178	.00515
24.12	.000048	.000169	.00034	.00077
23.04	.....	.0000117	.000044	.000151

Weights of HCl per 100 weights of H_2O	Partial pressure of HCl, mm. Hg		
	50°C.	60°C.	100°C.
76.6			
66.7			
58.3	825		
50.8	141		
44.5	35.7	625	
39.4	8.9	188	760
35.0	2.21	54.5	255
31.6	0.55	15.6	85
29.05	.135	4.66	30
27.04	.034	1.34	9.9
25.38	.0044	0.39	3.30
24.12	.0014	.095	0.93
23.04	.00140	.0245	.280

Enthalpy and phase-equilibrium data for the binary system HCl-H_2O are given by Van Nuys, *Trans. Am. Inst. Chem. Engrs.*, 38, 443 (1943).

Table 14-21.[11] Hydrogen Sulfide (H_2S)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	2.68	3.15	3.67	4.25	4.85	5.45	6.09	6.76

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	7.45	8.14	8.84	10.3	11.9	13.5	14.4	14.8

"International Critical Tables," vol. 3, p. 259.

Table 14-22.[2] Methane (CH_4)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	2.24	2.59	2.97	3.37	3.76	4.13	4.49	4.86

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	5.20	5.51	5.77	6.36	6.66	6.82	6.92	7.01

"International Critical Tables," vol. 3, p. 260.

Table 14-23.[2,3] Nitric Oxide (NO)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	1.69	1.95	2.18	2.42	2.64	2.87	3.10	3.51

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	3.52	3.72	3.90	4.18	4.36	4.48	4.52	4.54

"International Critical Tables," vol. 3, p. 259.

Table 14-24.[2,12,13] Nitrogen (N_2)[a]

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	5.29	5.97	6.66	7.36	8.04	8.65	9.24	9.85

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	10.4	10.9	11.5	12.0	12.5	12.6	12.6	12.6

"International Critical Tables," vol. 3, p. 256. See also Frey, Schweickert, and Minnick, *Ind. Eng. Chem.*, 44, 1146 (1952).

[a] Atmospheric nitrogen = 98.815 vol. % N_2 + 1.185 vol. % A.

Table 14-25.[10] Nitrogen (N_2)

Partial pressure of N_2, mm. Hg	$10^{-4} \times H$	
	19.4°C.	24.9°C.
900	8.24	9.08
2000	8.32	9.15
3000	8.41	9.25
4000	8.49	9.38
5000	8.59	9.49
6000	8.74	9.62
7000	8.86	9.75
8100	9.04	
8200	.....	9.91

See also Goodman and Krase [*Ind. Eng. Chem.*, 23, 401 (1931)] for values up to 169°C. and 300 atm.

Table 14-26.[14,17] Nitrous Oxide (N_2O)

t, °C	5	10	15	20	25	30	35
$10^{-4} \times H$	1.17	1.41	1.66	1.98	2.25	2.59	3.02

"International Critical Tables," vol. 3, p. 259.

Table 14-27.[2,12,13,15,16] Oxygen (O_2)

t, °C	0	5	10	15	20	25	30	35
$10^{-4} \times H$	2.55	2.91	3.27	3.64	4.01	4.38	4.75	5.07

t, °C	40	45	50	60	70	80	90	100
$10^{-4} \times H$	5.35	5.63	5.88	6.20	6.63	6.87	6.99	7.01

"International Critical Tables," vol. 3, p. 257. Frey, Schweickert, and Minnick [*Ind. Eng. Chem.*, 44, 1146 (1952)] give $H = 4.46 \times 10^{-4}$ at 25°C. and other values up to 345°C.

Table 14-28.[10] Oxygen (O_2)

Partial pressure of O_2, mm. Hg	$10^{-4} \times H$	
	25°C.	25.9°C.
600	.....	4.79
900	4.58	.....
2000	4.59	4.80
3000	4.60	4.85
4000	4.68	4.88
5000	4.73	4.92
6000	4.80	4.98
7000	4.88	5.05
8150	4.98	.....
8270	.....	5.16

"International Critical Tables," vol. 3, p. 257. See also *Trans. Am. Soc. Mech. Engrs.*, 76, 69 (1954) for solubility of O_2 for 100°F. < T < 650°F., 500 < P < 2000 lb./sq. in.

Table 14-29. Ozone (O_3)

t, °C	0	5	10	15	20	25	30	35	40	50
$10^{-4} \times H$	1.94	2.18	2.48	2.86	3.76	4.57	5.96	8.18	12.8	29.4

"International Critical Tables," vol. 3, p. 257.

Table 14-30.[18] Propylene (C_3H_6)

t, °C	2	6	10	14	18
$10^{-4} \times H$	3.04	3.84	4.46	5.06	5.69

"International Critical Tables," vol. 3, p. 260.

Table 14-31.[3] Sulfur Dioxide (SO_2)

Weight of SO_2 per 100 weights of H_2O	Partial pressure of SO_2, mm. Hg							
	0°C.	7°C.	10°C.	15°C.	20°C.	30°C.	40°C.	50°C.
20	646	657						
15	474	487	726					
10	308	417	474	562	690			
7.5	228	262	349	419	517	688		
5.0	148	198	226	270	336	452	665	
3.5	99	92	105	127	161	216	322	456
2.5	68	51	59	71	92	125	184	266
1.5	33.3	31	37	44	56	78	121	172
0.7	15.2	20.6	23.6	28.0	36.0	52	82	116
1	9.9	13.5	15.6	19.3	26.0	36	57	82.0
.5	5.1	6.9	7.9	10.0	14.1	19.7		
.2	2.8	3.7	4.6	5.7	8.5	11.8	.....	31.0
.15	1.9	2.6	3.1	3.8	5.8	8.1	12.9	20.0
.10	1.2	1.5	1.75	2.2	3.2	4.2	7.3	12.0
.05	0.6	0.7	0.75	0.8	1.2	1.7	2.8	4.7
.02	.25	.3	.3	.3	0.5	0.6	0.8	1.3

Table 14-32. Sulfur Dioxide (SO_2)

Weight of SO_2 per 100 weights of H_2O	Partial pressure of SO_2, mm. Hg						
	0°C.	10°C.	20°C.	25°C.	30°C.	40°C.	50°C.
15	500	735					
10	310	470	.....	840			
8	240	370	580	670	780		
6	175	270	430	505	590	770	
4	110	170	270	320	380	510	700
2	50	75	110	150	170	250	340
1	20	35	50	60	70	110	160

Neuell and Lieke, "Solubilities of Inorganic and Organic Compounds," p. 319, Van Nostrand, Princeton, N.J., 1952.

Table 14-33. Sulfur Dioxide (SO_2)

Weight of SO_2 per 100 weights of H_2O	Partial pressure, mm. Hg				
	20°C.	30°C.	70°C.	90°C.	110°C.
7.45	350	1243			
4.36	420	778	1272		
1.84	82.5	149	361	465	
0.51	.....	70.0	146	239	348

See Pearson, Lundberg, Watt, and McCarthey [*Chem. Eng. Progress*, 47, 257 (1951)] for a review of all available solubility data for SO_2 in H_2O.

References for Tables 14-2 to 14-33

1 Winkler, "Landolt-Bornstein Physikalisch-chemische Tabellen."
2 Winkler, *Ber.*, 34, 1408 (1901).
3 Sherwood, *Ind. Eng. Chem.*, 17, 745 (1925).
4 Breitenbach, *Bull. Univ. Wis. Eng. Exp. Sta., Ser.* 60.
5 Winkler, *Magyar Chemiai Folyoirat*, 4, 33 (1898).
6 Winkler, *Chem.-Ztg.*, 23, 687 (1899).
7 Bohr, *Ann. Physik*, 68, 500 (1899).
8 Sander, *Z. physik. Chem.*, 78, 513 (1912).
9 Winkler, *Z. physik. Chem.*, 9, 171 (1892).
10 Camuto, *Physik. Z.*, 5, 253 (1904).
11 Winkler, *Mathematikai és Természettudományi Értesítő, Budapest*, 25, 86 (1907).
12 Winkler, *Ber.*, 24, 89 (1891).
13 Winkler, *Math. naturw. Ber. Ungarn*, 9, 195 (1892).
14 Zeisberg, *Chem. & Met. Eng.*, 32, 326 (1925).
15 Winkler, *Ber.*, 24, 3602 (1891).
16 Geffcken, *Z. physik. Chem.*, 49, 257 (1904).
17 Knauth, *Phys. Rev.*, 19, 512 (1922).
18 Winkler, *Z. physik. Chem.*, 55, 344 (1906).
19 Winkler, *Ber.*, 22, 1764 (1889).
20 Thea, *Liebigs Ann. Chem.*, 123, 187 (1862).
21 Wiebe and Gaddy, *J. Am. Chem. Soc.*, 61, 315 (1939); 62, 815 (1940).
22 Adams and Edmonds, *Ind. Eng. Chem.*, 20, 447 (1937).

Table 14-34. Non-aqueous Solvents for Gas Absorption

Solutes:

Acetylene, C_2H_2	Hydrogen, H_2
Air	Hydrogen chloride, HCl
Ammonia, NH_3	Hydrogen sulfide, H_2S
Bromine, Br_2	Methane, CH_4
Carbon dioxide, CO_2	Methyl chloride, CH_3Cl
Carbon monoxide, CO	Nitric oxide, NO
Chlorine, Cl_2	Nitrogen, N_2
Ethane, C_2H_6	Nitrous oxide, N_2O
Ethylene, C_2H_4	Oxygen, O_2
	Sulfur dioxide, SO_2
	Etc.

Solvents:

Acetic acid (glacial), $C_2H_4O_2$	Ethyl acetate, $C_4H_8O_2$
Acetic anhydride, $C_4H_6O_3$	Ethyl alcohol, C_2H_6O
Acetone, C_3H_6O	Ethylene chloride, $C_2H_4Cl_2$
Amyl alcohol, $C_5H_{12}O$	Ethyl ether, $C_4H_{10}O$
Aniline, C_6H_7N	Methyl acetate, $C_3H_6O_2$
Benzene, C_6H_6	Methyl alcohol, CH_4O
Bromobenzene, C_6H_5Br	Nitrobenzene, $C_6H_5NO_2$
Carbon disulfide, CS_2	Propyl alcohol, C_3H_8O
Carbon tetrachloride, CCl_4	Propylene, C_3H_6
Chlorobenzene, C_6H_5Cl	Toluene, C_7H_8
Chloroform, $CHCl_3$	Etc.

Figures 14-1 and 14-2 give the solubility of ether in various solvents. All the solubility curves given with the exception of that for butyl alcohol are for 20°C. The butyl alcohol curve is for 15°C. (Robinson, "Recovery of Volatile Solvents," pp. 154–156, Reinhold, New York, 1922.)

Carbon Dioxide and Hydrogen Sulfide in Aqueous Ammonia. When carbon dioxide dissolves in an aqueous ammonia solution the following ionic equilibria are established:

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4^+ + HCO_3^- \quad (a)$$
$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \quad (b)$$
$$NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^= \quad (c)$$

Van Krevelen, Hoftijzer, and Huntjens [*Rec. trav. chim.*, 68, 193 (1949)] have shown how mass-action expressions and nitrogen, carbon, and ion balances can be combined to represent the composition of the solution and the equilibrium partial pressures of NH_3 and CO_2. The mass-action constants vary with temperature and ionic strength. Figures 14-3 and 14-4 give typical calculated results. Figure 14-3 shows the variation of

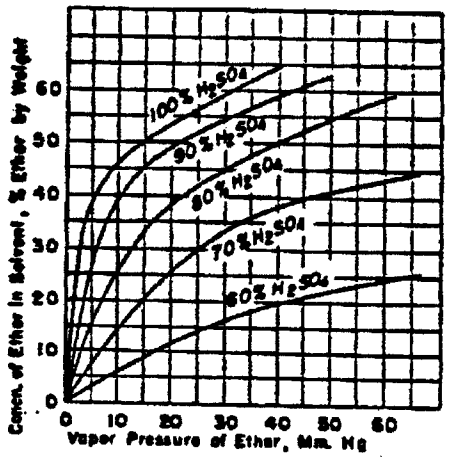

FIG. 14-1. Vapor pressure of ether at 20°C. from H_2SO_4 solutions of several concentrations of H_2SO_4 and H_2O.

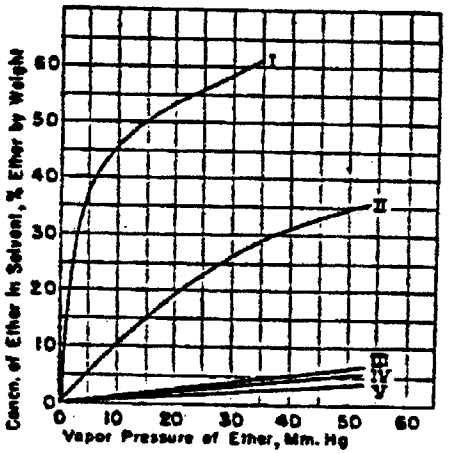

FIG. 14-2. Vapor pressure of ether from its solution in several solvents.

Curve	Solvent	Temp., °C.
I	100% H_2SO_4	20
II	m-Cresol	20
III	Amyl alcohol	20
IV	Butyl alcohol	15
V	Ethyl alcohol	20

the dissolved components as a function of R, the ratio of atoms of total dissolved carbon to atoms of dissolved nitrogen at 20°C. Figure 14-4 shows calculated partial pressures as a function of R and total ammonia concentration n at the same temperature. The calculated results agree closely with the experimental data of van Krevelen *et al.*, as well as with data of Preston and Badger [*J. Soc. Chem. Ind.*, 57, 106 (1938)]. Badger and Silver [*J. Soc. Chem. Ind.*, 57, 110 (1938)]. Badger [*J. Soc. Chem. Ind.*, 57, 112 (1938)]. Badger and Wilson [*J. Soc. Chem. Ind.*, 66, 54 (1947)], and Dryden [*J. Soc. Chem. Ind.*, 66, 59 (1947)].

Solution of hydrogen sulfide in aqueous ammonia involves the ionic reaction

$$NH_3 + H_2S \rightleftharpoons NH_4^+ + HS^- \quad (d)$$

DRAFT

9/22/95

Spoke with Bryan Newell

Determine amount (ppmv) of CH_4 in headspace.

Partial pressure of the gas (Pg) is the decimal fraction of the headspace amount.
OR divide ppmv value by 1000000.

follow rest of calculations as outlined in the SOP.

Reporting Limit = 0.00024 or 1.0 ppmv for methane