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Solubilities of Gases in Simulated Tank 241-SY-101 Wastes

**J. D. Norton
L. R. Pederson**

September 1995

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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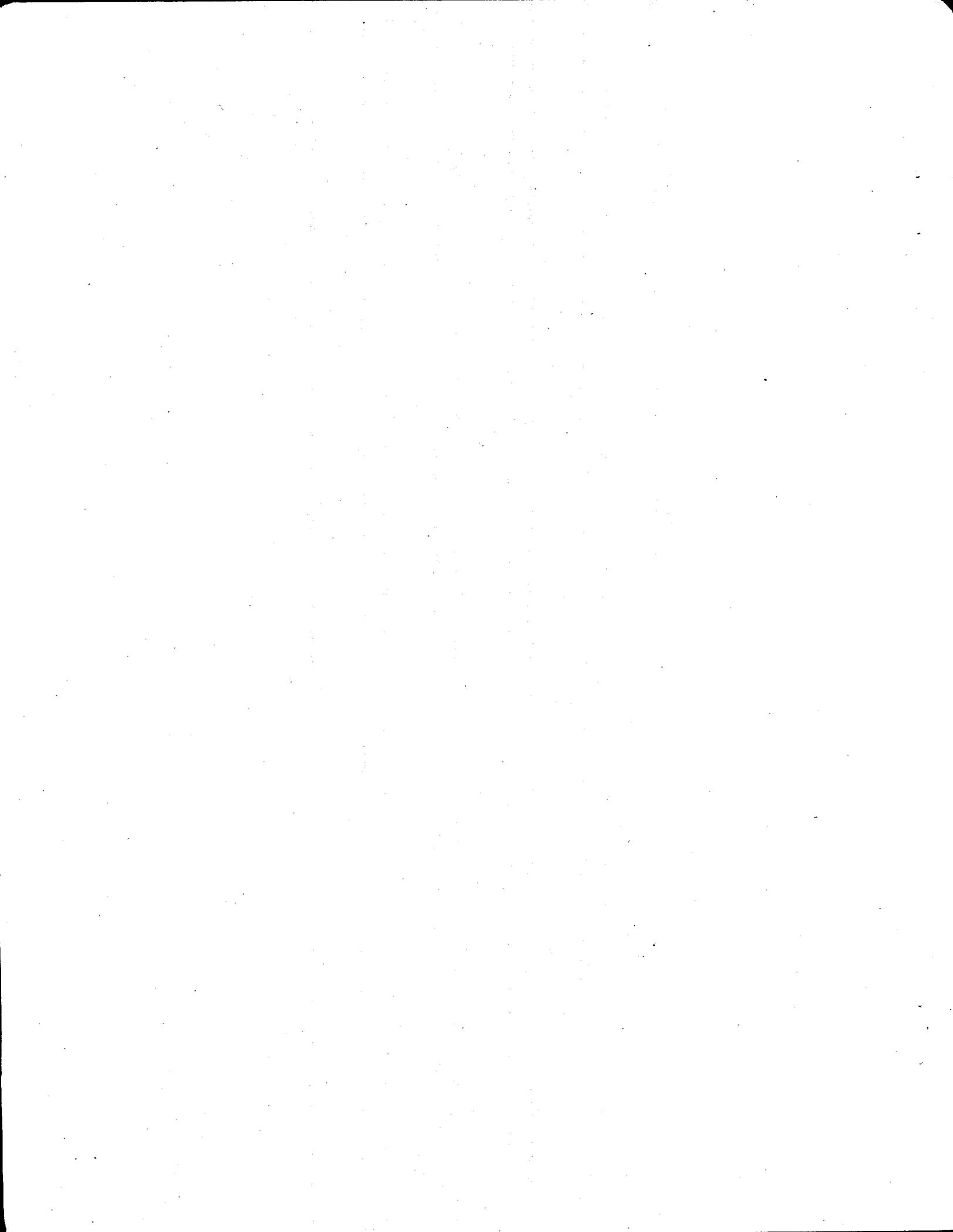
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Summary

Oxygen, nitrogen, hydrogen, methane, and nitrous oxide solubilities were evaluated as a function of temperature in SY1-SIM-93B, a homogeneous simulated waste mixture containing sodium hydroxide, sodium nitrite, sodium nitrate, sodium aluminate, and sodium carbonate, the principal inorganic constituents of the wastes in Tank 241-SY-101. Ammonia solubility data for this simulated waste was obtained as a function of temperature in an earlier study. The choice of a homogeneous waste mixture in this study has the advantage of eliminating complications associated with a changing electrolyte concentration as a function of temperature that would be encountered with a slurry simulant. Dissolution is one of the means by which gases may be retained in Hanford Site wastes. While models are available to estimate gas solubilities in electrolyte solutions, few data are in existence that pertain to highly concentrated, multicomponent electrolytes such as those stored in Hanford Site waste tanks.

Laboratory equipment was designed and constructed with the assistance of the Westinghouse Hanford Company (WHC) 200W Glass Shop to allow the volume of gases dissolved to be measured directly, without the reliance on calculation of uptake volumes based on pressure/volume relationships. A two-chambered sample vessel was an essential feature of the solubility apparatus, which avoided artifacts associated with the local condensation and re-equilibration of water vapor. Most of the apparatus was submerged in a well-stirred water bath to maintain thermal equilibrium within $\approx 0.1^\circ\text{C}$. The apparatus was capable of measuring gas uptake volumes as small as a few tenths of a mL, a necessary feature when working with concentrated electrolytes, where solubilities are much reduced when compared to those in pure water.

Experimentally determined gas solubilities were compared with literature models wherever possible. The Pitzer ion interaction model (Pitzer 1987; 1990), a modified Pitzer model (Pasamehmetoglu et al. 1994), and the Schumpe model (Schumpe 1993; Hermann, Dewes, and Schumpe 1995) were considered in this study, each of which utilizes specific interaction parameters that are derived from experimental data, usually for solutions containing one electrolyte. Each of these models constitutes a refinement of the Sechenov Equation, which provides a simple description of the lowering of gas solubilities in electrolyte solutions ("salting-out effect"). A significant shortcoming of literature models was the lack of data on the temperature dependence on interaction parameters (with the exception of Pitzer model parameters for oxygen).

Oxygen solubilities in the simulated waste mixture were lowered by approximately a factor of 10 relative to those in pure water. Experimentally determined oxygen solubilities in the simulant were in relatively good agreement with both the Pitzer model and with the Schumpe model. Clegg and Brimblecombe (1990) have given detailed Pitzer ion interaction parameters for oxygen, including a first-order temperature dependence of the interaction terms; this gave the best fit to present data. The Schumpe model (Hermann, Dewes, and Schumpe 1995) agreed very well with the Pitzer model (used with ion interaction parameters from Clegg and Brimblecombe 1990) at low temperatures, but tended to slightly underestimate oxygen solubilities at higher temperatures.

For hydrogen, solubilities were smaller in the simulant by approximately a factor of 5 to 7 compared to pure water. Experimental hydrogen solubilities were reasonably well described by the Schumpe model, but were considerably smaller than predictions of the modified Pitzer model

(Pasamehmetoglu et al. 1994). No detailed Pitzer ion interaction parameters, including a temperature dependence, were available for hydrogen in multicomponent electrolyte solutions.

Nitrogen was approximately a factor of 10 less soluble in the simulated waste mixture than in pure water. Experimentally determined nitrogen solubilities also were well described by the Schumpe model. As was the case for hydrogen, the modified Pitzer model led to an overestimate of the expected solubility by approximately a factor of 3. Detailed Pitzer ion interaction parameters, including a temperature dependence, were not available for nitrogen dissolved in concentrated, multicomponent electrolyte solutions.

Methane solubilities were also lowered in the simulated waste mixture by approximately a factor of 10 compared to solubilities in pure water. Parameters were available only for the Schumpe model, which provided solubility estimates in reasonably good agreement with experimental results.

Nitrous oxide solubilities were a factor of 5 to 7 times less in the simulated waste mixture than in pure water. Agreement with predictions of the Schumpe model were good. Nitrous oxide is the most soluble of the five gases included in this study, by 1 to 2 orders of magnitude.

Of all the gases considered in this study, ammonia solubilities were the least affected by the presence of electrolytes, diminishing by approximately a factor of 2 in the simulated waste compared to pure water. At 25°C, the Pitzer model (Clegg and Brimblecombe 1989) the Schumpe model (Hermann, Dewes, and Schumpe 1995) and a modified Pitzer model (Pasamehmetoglu et al. 1994) were all in good agreement with experimental values. The three models tended to underestimate ammonia solubilities at higher temperatures, however.

Inventories of gases that could be dissolved in the wastes contained in Tank 241-SY-101 were estimated, based on experimentally determined solubilities from this study in combination with the Schumpe model and the modified Pitzer model. Estimations were based on the mother liquor of the wastes present in Tank 241-SY-101 rather than on the composition of the composite wastes. It was assumed in these calculations that the entire waste was in equilibrium with gas bubbles trapped in the lower, non-convecting layer, certainly a conservative assumption. For oxygen, it was assumed that the waste tank was fully equilibrated with air, also very conservative. For all but nitrous oxide and ammonia, the total estimated inventory of dissolved gases was very small, less than 100 SCF for the entire tank, based on the Schumpe model and gas-specific interaction parameters modified to be consistent with present solubility data. The total quantity of nitrous oxide that could be dissolved in the entire waste tank is approximately equal to 10% of that released in a typical gas release event. The ammonia concentration in Tank 241-SY-101 wastes has been estimated to 0.6 weight % by Norton and Pederson (1994), based on solubility behavior.

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1.0 Introduction

Mixed chemical and radioactive wastes remaining from defense materials production activities are currently stored in large underground tanks at the Hanford Site. Some of these wastes are in the form of a thick, multi-component slurry. Among the components are sodium hydroxide, sodium aluminate, sodium nitrate, sodium nitrite, sodium carbonate, organic complexants, buffering agents, partial decomposition products of organic complexants, transition metal salts, and various minor and trace compounds (see for example, Herting et al. 1992a; 1992b).

Certain gaseous decomposition products are known to be produced in these wastes from radiolytic and thermal processes (Babad et al. 1991; Ashby et al. 1992; DOE 1994). Among those products are ammonia, nitrous oxide, nitrogen, hydrogen, and methane. Oxygen is well-known to be produced by water radiolysis as well (Meisel et al. 1991), but is expected to be consumed in reactions with organic waste components (Ashby et al. 1992). Gases are retained in and periodically released from some of these wastes, of which Tank 241-SY-101 is perhaps the best known. The emplacement of a mixer pump has eliminated gas buildup and release cycles in that tank (DOE 1994).

The primary means by which gases may be retained in the concentrated Hanford Site tank wastes is as bubbles trapped within a non-convecting layer having a relatively high solids loading. The bubbles may be attached to solid particles in response to interfacial tension forces or as dendritic bubbles held in place by liquid lamellae that form in narrow pore throats between solid particles (Bryan, Pederson, and Scheele 1992; Gauglitz et al. 1994). Except for ammonia, most gases that are formed from radiolytic and thermal processes are only weakly soluble in the concentrated waste mixtures. Dissolved gases other than ammonia are thus expected to comprise only a small fraction of gases retained in concentrated Hanford Site wastes (Allemann 1994; Pasamehmetoglu et al. 1994). Little experimental data on gas solubilities in solutions similar to those present in Hanford Site tank wastes are in existence, however.

The solubilities of many gases in aqueous solutions can be adequately described by Henry's Law, which states that the vapor pressure of a dilute solute is directly proportional to the concentration of the solute (Andrews 1971). Henry's Law is an infinite dilution approximation, typically accurate for gas pressures up to 5 to 10 atmospheres and dissolved gas mole fractions up to approximately 0.03 (Andrews 1971). The Henry's Law constant may be defined:

$$K_H(i) = \gamma_i m_i / f_i \approx \gamma_i m_i / p_i \quad (1)$$

where $K_H(i)$ is the Henry's Law constant for gas i (moles/kg solvent-atmosphere), γ_i is the activity coefficient for gas i in the aqueous solution, m_i is the concentration of gas i in water (moles/kg water), and f_i is the fugacity of that gas. Fugacity may be replaced by the partial pressure p_i (atm) for essentially ideal gas mixtures. For dilute gases dissolved in pure water, $\gamma_i \approx 1$. In aqueous solutions containing dissolved electrolytes such as Hanford Site tank wastes, gas solubilities are well known to be lower than those in pure water and $\gamma_i > 1$. The challenge in describing gas solubilities in concentrated electrolyte solutions such as Hanford Site tank wastes is to define values for γ_i .

The influence of electrolyte concentration on the solubility of a sparingly soluble gas was first described by Sechenov (1889):

$$\log (c_{G,O}/c_G) = K_{Sechenov} m_s \quad (2)$$

where $c_{G,O}$ is the solubility of a particular gas in pure water, c_G is the solubility of that same gas in the presence of a dissolved salt, m_s is the concentration of a dissolved salt, and $K_{Sechenov}$ is the Sechenov constant. The Sechenov constant $K_{Sechenov}$ is specific to a particular gas, a particular electrolyte, and is also temperature-dependent. The activity coefficient $\gamma_{i,electrolyte}$ may be calculated from the relative solubilities of a gas in pure water and in an electrolyte solution:

$$\gamma_{i,electrolyte} = \gamma_{i,water} c_{G,O}/c_G \quad (3)$$

Methods to estimate the Sechenov constant for various common salts in water have been described (for example, see Pawlikowski and Prausnitz 1983). While successfully describing trends in gas solubilities as a function of electrolyte concentration up to approximately 0.1 molal, Equation (2) tends to overestimate the salting-out effect (lowering of solubility) at high electrolyte concentrations (Schumpe 1993). Equation (2) also is not directly applicable to mixed electrolyte solutions such as those found in Hanford Site waste tanks.

Modifications to the Sechenov Equation have allowed its extension to mixed electrolyte solutions (Schumpe 1993; Hermann, Dewes and Schumpe 1995):

$$\log (c_{G,O}/c_G) = \Sigma (h_{ion} + h_g) c_i \quad (4)$$

where h_{ion} represents a set of ion-specific parameters, h_g represents a set of gas-specific parameters, and c_i is the molar concentration of the specific ion. However, ion-specific and gas-specific parameters, which are certainly expected to vary with temperature, were given only for a temperature of 298.2K (Hermann, Dewes, and Schumpe 1995). The applicability of Equation (4) to solutions with high electrolyte concentrations has not been established.

The Pitzer ion interaction model is among the more successful methods devised to estimate gas solubilities in mixed electrolytes (Pitzer 1987; 1990). This model requires the use of a relatively large set of binary and ternary interaction parameters that are derived from experimental data to calculate the activity coefficient γ_i for the gas being dissolved in a solution containing electrolytes. A simplified expression has been given by Clegg and Brimblecombe (1990) for slightly soluble gases (no self-interaction terms):

$$\ln \gamma_i = \Sigma \lambda_{ic} m_c + 2 \Sigma \lambda_{ia} m_a + \Sigma \Sigma m_c m_a \zeta_{ica} + \Sigma \Sigma m_c m_c \eta_{icc} + \Sigma \Sigma m_a m_a \eta_{iaa} \quad (5)$$

where subscripts i , c , and a represent neutrals (gas being absorbed), cations, and anions, respectively; and λ_{ij} , ζ_{ijk} , and η_{ixx} are interaction parameters that must be determined from experimental data. Interaction parameters for all of the components of Hanford Site tank wastes, however, have not yet been established. Hanford Site waste mixtures are generally more concentrated than solutions from which existing ion interaction parameters were derived.

Estimates of nitrous oxide, ammonia, hydrogen, and nitrogen solubilities in Hanford Site tank wastes have been made using the Edwards et al. (1978) modification to the Pitzer ion interaction model (Pasamehmetoglu et al. 1994). These estimates were made by defining an "average" salt-salt interaction parameter, assuming that the best fit for a large number of salts yields parameters that approximate the hypothetical average salt. For a 1-1 electrolyte, the following expression has been given (Pasamehmetoglu et al. 1994):

$$\ln \gamma_i = 2 \beta_{0, is} m_s + \beta_{1, is} [1 - (1 + 2\sqrt{m_s}) \exp(-2(\sqrt{m_s}))] + \frac{\beta_{1, ss}}{4} [-1 + (1 + 2\sqrt{m_s} + 2m_s) \exp(-2\sqrt{m_s})] \quad (6)$$

where m_s is the molal concentration of salt (moles/kg water), $\beta_{0, is}$ (kg water/mole) and $\beta_{1, is}$ are gas-salt interaction parameters, and $\beta_{1, ss}$ is the salt-salt interaction parameter. This latter term is independent of the identity of the gas species. Pasamehmetoglu et al. (1994) determined a value for $\beta_{1, ss}$ by averaging results for sixty 1-1 electrolytes at 25°C, and obtained a value of 0.17. From an analysis of available literature data on gas solubility in electrolytes, values of $\beta_{0, is}$ and $\beta_{1, is}$ were given for hydrogen, nitrogen, nitrous oxide, and ammonia, given in Table 1.1. Few laboratory data on gas solubilities in complex waste mixtures were available, so a comparison of calculated and measured solubilities was not possible.

The solubility of ammonia in simulated Tank 241-SY-101 mixtures and in sodium hydroxide solutions has been studied by Norton and Pederson (1994), and Henry's Law constants determined as a function of temperature. The solubility of ammonia in the homogeneous simulant SY1-SIM-93B was approximately half of that in pure water, when normalized to the quantity of water present in the simulant. Ammonia solubility in the slurry simulant SY1-SIM-91A was approximately a factor of 8 less than in pure water at 30°C and approximately a factor of 4 less at 70°C. Experimental results for sodium hydroxide solutions and for the homogeneous simulated waste mixture were in reasonably good agreement with predictions of the Pitzer ion interaction model. Ion interaction parameters were not available for all ions present in the wastes, however, requiring estimations to be made in modelling Henry's Law constants (Norton and Pederson 1994). Good agreement between experimental data reported by Norton and Pederson (1994) and values calculated using Equation (6) and ammonia-specific parameters given in Table 1.1 were also obtained by Pasamehmetoglu et al. (1994).

Table 1.1. Gas Interaction Parameters for Hypothetical Average Salt, with $\beta_{1, ss} = 0.17$ (from Pasamehmetoglu et al. 1994)

Gas	$\beta_{0, is}$	$\beta_{1, is}$
H ₂	0.0531	0.2644
N ₂	0.0531	0.2644
N ₂ O	0.0466	0.3692
NH ₃	0.0375	0.2997

In this study, the solubilities of nitrous oxide, nitrogen, hydrogen, oxygen, and methane in a simulated waste mixture were measured as a function of temperature. From these data, Henry's Law constants and activity coefficients for each of the gases in the electrolyte solution were calculated. Organic waste components were omitted from the simulant mixtures to avoid complications associated with gas generation. Comparisons of laboratory data to the Pitzer ion interaction model and to the Sechenov equation as modified by Schumpe and coworkers were made.

2.0 Experimental Methods

2.1 Waste Simulant Compositions

Gas solubilities were evaluated in the simulant SY1-SIM-93B, a homogeneous solution. This simulant was formulated based on the composition of wastes stored in Tank 241-SY-101 (Herting et al. 1992a; 1992b), and contained sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, and sodium carbonate. The compositions and methods of preparation of this and other simulants have been described by Bryan and Pederson (1994). No organic components were added to these mixtures to avoid complications associated with gas generation reactions. The composition of the simulant is given in Table 2.1. In Table 2.2, the composition is given in molar and molal units.

2.2 Solubility Measurements

Solubilities of nitrous oxide, nitrogen, oxygen, hydrogen, and methane were evaluated as a function of temperature in simulated waste mixtures. Gas solubility measurements were made using the apparatus shown in Figure 2.1. The apparatus is also shown schematically in Figure 2.2a to 2-2d. This apparatus allowed a direct measure of the volume of gas uptaken by a liquid sample to be measured at a given pressure, without requiring calculation of the uptake volume based on pressure/volume relationships.

Table 2.1. Composition of Homogeneous Simulant SY1-SIM-93B

Form of Components Used to Prepare Simulant	M (mole/L)	Weight %	Form of Components in Simulant Mixture	Weight %
NaOH	3.4	11.2	NaOH	5.5
Al(NO ₃) ₃ ·9H ₂ O	0.43	13.3	NaAlO ₂	2.9
NaNO ₃	0.40	2.8	NaNO ₃	11.8
NaNO ₂	2.0	11.4	NaNO ₂	11.4
Na ₂ CO ₃	0.20	1.8	Na ₂ CO ₃	1.8
H ₂ O		59.6	H ₂ O	66.6
Total		100.1		99.9
Density	1.18 g/cm ³			

Table 2.2. Composition of Simulant SY1-SIM-93B in Molar and Molal Concentration Units

Component	M (mole/L)	m (mole/kg water)
Na ⁺	6.02	7.65
OH ⁻	1.62	2.06
AlO ₂ ⁻	0.42	0.53
NO ₃ ⁻	1.63	2.08
NO ₂ ⁻	1.95	2.48
CO ₃ ²⁻	0.20	0.25

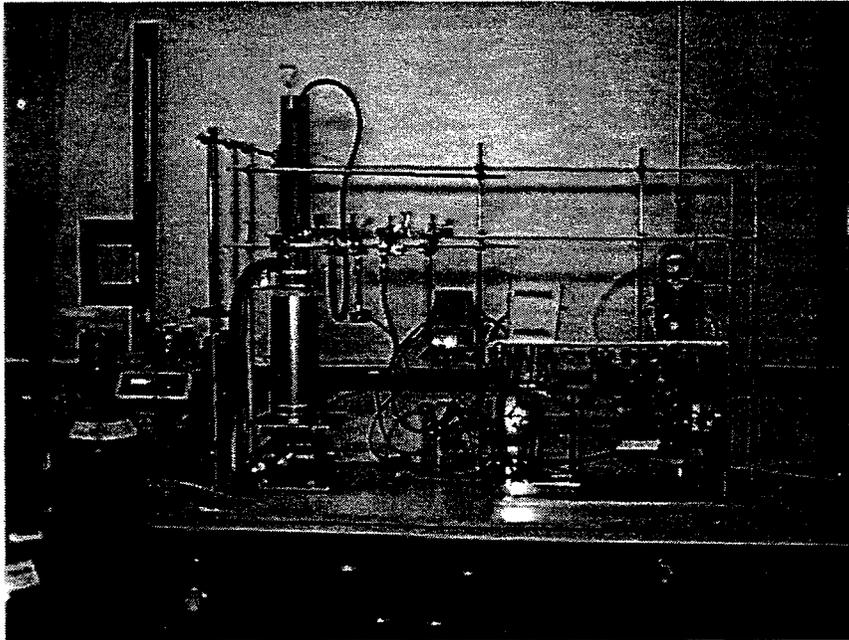


Figure 2.1. Gas Solubility Apparatus Utilized in This Study. The apparatus is shown schematically in Figures 2.2a to 2.2d.

2.2.1 Apparatus Description

The gas solubility apparatus consisted of four main sections: (1) a vacuum manifold (Figure 2.2a); (2) gas burets (Figure 2.2b); (3) null pressure manometer (Figure 2.2c); and (4) sample vessels (Figure 2.2d). The apparatus was constructed principally from 13 mm od Pyrex[®] glass (Corning Glass, Corning, New York). Valves were purchased from Kontes Scientific Glassware (Vineland, New Jersey). These valves consisted of a glass body, a Teflon[®] (E. I. duPont de Nemours and Co., Wilmington, Delaware) plunger adjustable with a screw-type apparatus, and a polymer O-ring seal.

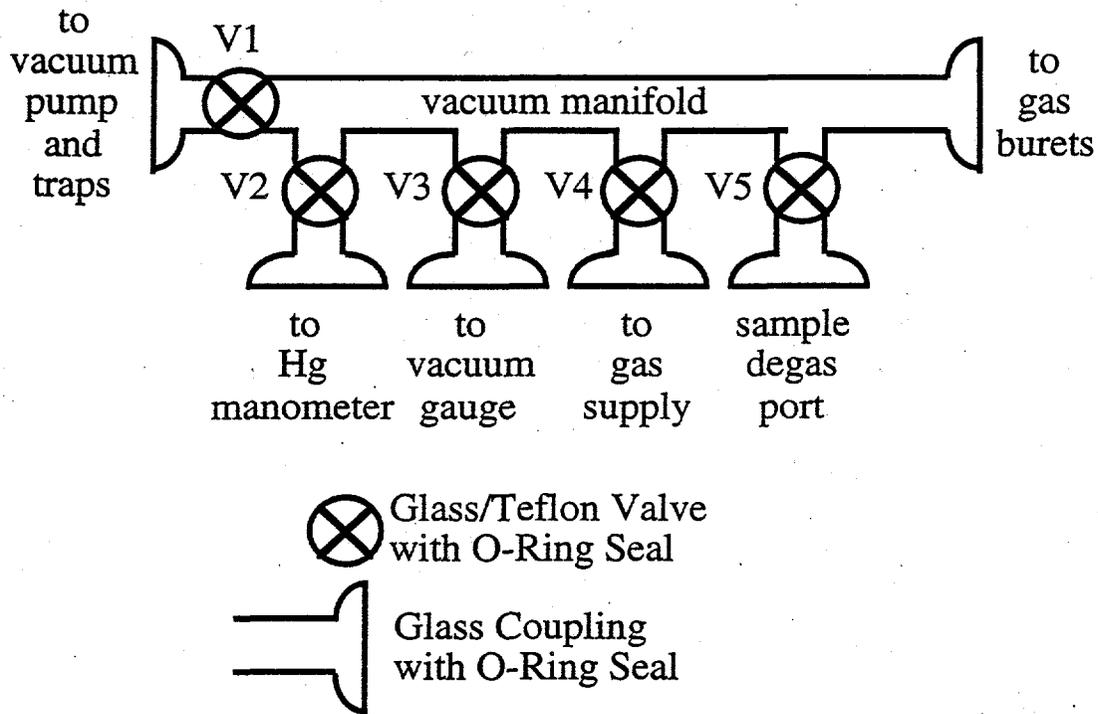


Figure 2.2a. Vacuum Manifold Portion of the Gas Solubility Apparatus Shown in Figure 2.1

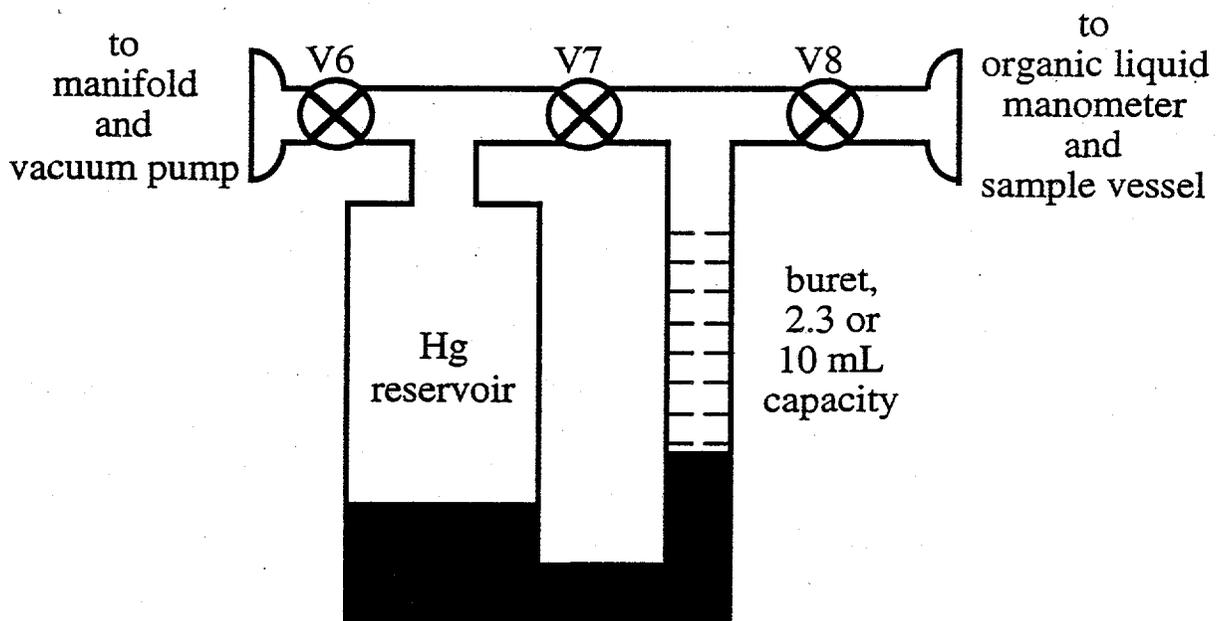


Figure 2.2b. Gas Buret Portion of the Gas Solubility Apparatus Shown in Figure 2.1

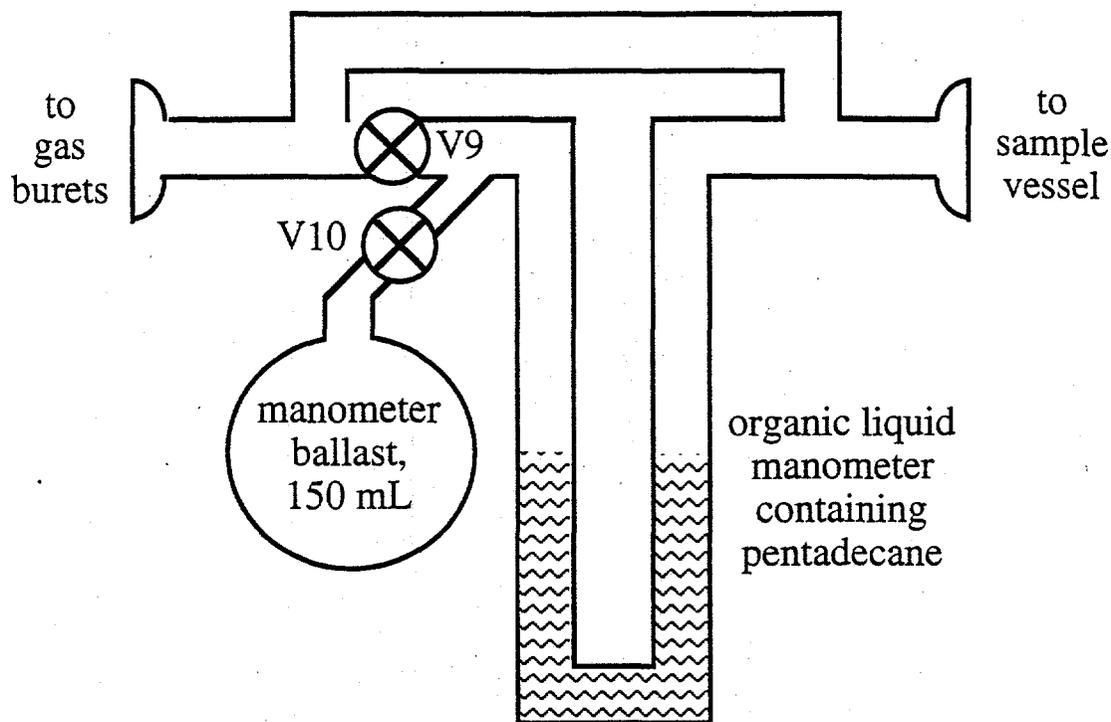


Figure 2.2c. Null-Pressure Manometer Portion of the Gas Solubility Apparatus Shown in Figure 2.1

Glass couplings were also purchased from Kontes, and utilized a polymer O-ring seal. Much of the apparatus was constructed at Westinghouse Hanford Company's 200W Area Glass Shops.

2.2.1.1 Vacuum Manifold (Figure 2.2a)

This section consisted of a mercury manometer (readable to 0.3 mm Hg), an electronic vacuum gauge (Granville-Phillips Model 275, Boulder, Colorado, for indication only), gas inlet, and a sample degas port. An Edwards Model 18 (Sussex, England) two-stage, direct-drive vacuum pump was connected to the vacuum manifold through a liquid nitrogen-cooled trap. An ultimate pressure of less than 10^{-3} Pa ($\approx 10^{-5}$ torr) could be achieved with this equipment.

2.2.1.2 Gas Burets (Figure 2.2b)

Two gas burets were included in this apparatus: one with a 2.3 mL maximum capacity readable to 0.01 mL, and one with a 10.00 mL capacity readable to 0.03 mL. Only one gas buret could be used at any one time.

2.2.1.3 Null-Differential Pressure Manometer (Figure 2.2c)

The null-differential pressure manometer was used to ensure that the starting gas pressure was maintained throughout the gas uptake experiment. Constructed of ≈ 3 mm id glass tubing, the null-differential pressure manometer contained pentadecane as the pressure indicator. Pentadecane was

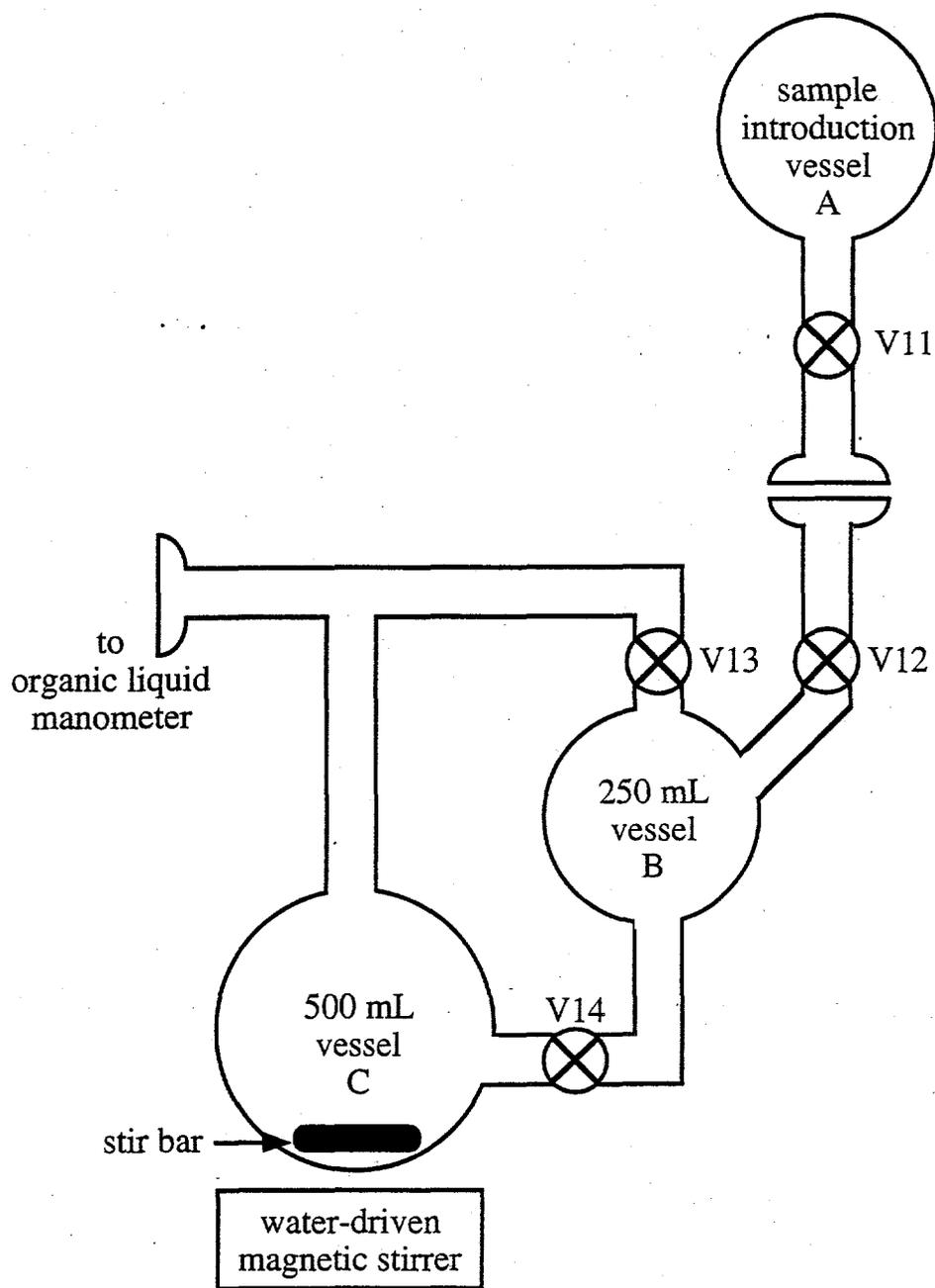


Figure 2.2d. Sample Vessel Portion of the Gas Solubility Apparatus Shown in Figure 2.1

chosen because of its low density and therefore high sensitivity to small changes in pressure, low chemical reactivity, and low tendency to dissolve gases of interest to this study. A ballast bulb with a 150 mL capacity was added to improve the sensitivity of the manometer, by maintaining an approximately constant pressure on the left side of the manometer even while the liquid levels changed due to gas uptake. Without the ballast bulb in place (or with valve V10 closed), a drop in the liquid level on the left side of the manometer would also lower the pressure on that side, thereby resisting changes in liquid level.

2.2.1.4 Sample Vessels (Figure 2.2d)

This section consisted of a sample introduction vessel and a two-chambered apparatus in which the sample is held during gas uptake. This two-chambered sample apparatus is a variation of that described originally by Markham and Kobe (1941). The principal advantage of this structure is that an equilibrium water vapor pressure can be achieved and maintained throughout the gas uptake measurement. A Teflon-coated stirring bar and a water-driven magnetic stirrer sped the attainment of equilibrium without sample heating.

Initial tests were performed using a sample vessel quite different from that shown in Figure 2.2d. In the initial tests, the sample vessel consisted of a single Schlenk flask separated from the null differential pressure manometer and the rest of the apparatus by a water-cooled condenser. The purpose of the condenser was to maintain the partial pressure of water at a value lower than that of pure water at the bath temperature. Without the condenser, distillation of water from the brine sample to other parts of the apparatus would occur, particularly when the sample temperature was well above that of the water bath. Substantial measurement artifacts were encountered when using a single Schlenk flask and a water-cooled condenser, particularly when gas was admitted to the sample chamber. It is believed that measurement artifacts were the result of an initial water vapor compression and resulting condensation, followed by the re-establishment of an equilibrium water vapor pressure throughout the apparatus. When a gas stream was admitted to the sample vessel, water vapor was momentarily compressed ahead of a gas pressure plug. Water vapor was converted to liquid as it passed through the cool condenser at a transient pressure elevated above the equilibrium value. The result was that gas uptake by the sample was partially obscured by the re-establishment of the equilibrium water vapor pressure. These artifacts were of a similar magnitude as the solubility of various gases in concentrated simulated waste mixtures, but would have been of minor importance in studies of gas solubilities in pure water or dilute electrolytes.

2.2.1.5 Water Bath

The temperature of the gas burets, null-differential pressure manometer, and sample vessels were maintained to within 0.1°C in a water bath constructed of polymethyl methacrylate. Temperatures were maintained using two VWR Scientific Model 1120 water heater recirculators, one of which was used to also drive the magnetic stirrer. The water bath was equipped with a cover to minimize water evaporation during gas uptake measurements, particularly necessary at temperatures greater than $\approx 40^\circ\text{C}$.

2.2.2 Experimental Procedure

2.2.2.1 Sample Degassing

Simulant samples were degassed thoroughly before solubility measurements under vacuum. Approximately 300 mL of simulated waste was transferred into the sample introduction vessel (vessel A, 500 mL capacity). This vessel was connected to the vacuum manifold through valve V4. Four cycles of evacuation for approximately 15 seconds each at room temperature was found to be an effective degas procedure, with minimal water loss from the sample. Freeze-thaw cycles were also used. In this case, the sample was frozen in liquid nitrogen and then warmed while being evacuated. While freeze-thaw cycles worked well for pure water, they were not effective for concentrated brines. With valve V11 closed, the sample introduction vessel was then removed from the vacuum manifold and moved to a position adjacent to valve V12.

2.2.2.2 Apparatus Preparation

The entire apparatus, with the exception of the sample introduction vessel A, was evacuated to approximately 10^{-3} Pa. All valves except for V4, V5, and V11 were in the open position during this step. Evacuation continued for at least 10 minutes to facilitate removal of condensed water. This residual gas pressure is at least 7 orders of magnitude smaller than the typical working pressure of gases for which solubilities were determined. Residual gases should thus have had no measurable impact on later gas solubility measurements.

2.2.2.3 Sample Introduction

After thoroughly degassing the sample vessels and the rest of the apparatus, valve V8 was closed. At this point, valves V12, V13, and V14 remained open. Valve V11 was then partially opened to allow typically 2 to 3 mL of simulant to flow into vessel B and subsequently into vessel C, both of which remained under vacuum. Valves V13 and V14 were then closed. This small introduction of sample into vessel C enabled the sample vessels and the null-differential pressure manometer to reach the equilibrium water vapor pressure for the simulant. It is not necessary to know the precise volume of this simulant transfer to vessel C.

Vessel B was then completely filled with simulant by opening valve V11 (valves V13 and V14 were closed; valve V12 was open). The capacity of vessel B had been previously carefully calibrated by weighing the quantity of pure water necessary to completely fill the area bounded by valves V12, V13, and V14. Valve V12 was left open until the simulant sample was fully thermally accommodated with the water bath, requiring at least 1 hour. Premature closure of valve V12, when the simulant contained in vessel B remained cooler than the surrounding water bath, was definitively shown to result in catastrophic failure of the sample vessel assembly. The sample was left in vessel B until gas loading and equilibration was completed.

2.2.2.4 Gas Loading

A gas source (nitrous oxide, nitrogen, oxygen, hydrogen, or methane) was attached to the vacuum manifold through valve V4. Valve V2 to the Hg manometer and V3 to the electronic vacuum gauge

were opened, and valve V1 to the vacuum pump was closed. Gas was admitted to bring the system pressure up to approximately 600 mm Hg (80 kPa). Valve V4 was then closed, valve V1 opened, and the system evacuated to approximately 10^{-3} Pa (10^{-5} mm Hg). If a particular gas was being attached to the manifold for the first time, this bleed-in, pump-out procedure was repeated three times. The gas was then re-admitted to the apparatus to the final desired pressure (usually 100 to 600 mm Hg, or 13 to 80 kPa). At this point, the gas was in contact with the small amount of sample in the bottom of vessel C, but not to sample contained in vessel B. The apparatus was allowed to thermally equilibrate overnight.

2.2.2.5 Gas Uptake Measurement

Valve V9 on the null-differential pressure manometer and valve V7 on the gas buret were closed. The gas pressure indicated by the Hg manometer was noted and recorded. The Hg level on the gas buret was also noted and recorded. Valves V13 and V14 were then opened, allowing the sample to flow from vessel B to vessel C and be exposed to the gas. Additional gas was admitted to the apparatus through valve V4 to maintain a level reading at the null-differential pressure manometer. When no further changes could be observed (typically requiring 4 to 8 hours), the Hg level on the gas buret was noted and recorded. The initial gas buret reading was subtracted from the final reading to obtain the volume of gas uptaken by the simulant sample.

3.0 Solubility Results and Comparison to Calculated Solubilities

Solubilities of oxygen, hydrogen, nitrous oxide, nitrogen, and methane were measured as a function of temperature in simulated tank wastes. All except oxygen are known products of thermal and/or radiolytic reactions occurring in Tank 241-SY-101 and in other similar wastes by inference. These gases are either non-polar or weakly polar.

3.1 Oxygen

Oxygen solubilities were determined as a function of temperature in the homogeneous simulant SY1-SIM-93B, given in Table 3.1. The number enclosed by parentheses in the second column of Table 3.1 indicates the number of determinations made at that temperature. Uncertainties represent one standard deviation. Where only two determinations were made for a particular temperature, the standard deviation was estimated based on data obtained at other temperatures. As expected, oxygen solubilities in the simulated wastes were considerably smaller than in pure water, being lowered by a factor of eight to ten.

Oxygen solubilities in pure water are well established (Battino et al. 1981; 1982). An expression for the Henry's Law constant has been given (Benson et al. 1979; Battino et al. 1981):

$$\ln (K_{H, \text{oxygen}}) = 0.298399 - 5.59617 \times 10^3/T + 1.049668 \times 10^6/T^2 \quad (7)$$

where T is the temperature (K). The parameter K_H (mole/kg water-atm oxygen) is defined in Equation (1). Henry's Law constants calculated from Equation (6) for oxygen solubility in pure water are included in Table 3.1.

Oxygen solubilities in multicomponent brines are estimated by two related approaches: (1) the Schumpe method (Schumpe 1993; Hermann, Dewes, and Schumpe 1995), and (2) the Pitzer ion interaction model (Pitzer 1987; 1990). Schumpe and coworkers have assembled a set of ion-specific parameters h_{ion} and gas-specific parameters h_g for use with Equation (4), which are given for key components of simulated wastes in Appendix A. The scale devised by Schumpe (1993) for the gas-specific parameters h_g is arbitrarily referenced to a value for oxygen of 0.0000 m³/kg. Clegg and

Table 3.1. Oxygen Solubility in Simulant SY1-SIM-93B

Temperature, °C	Volume Dissolved per Liter Simulant (STP)	Volume Dissolved per kg Simulant (STP)	Henry's Law Constant, mole/kg water-atm	Henry's Law Constant for Pure Water, mole/kg water-atm
29.8	2.48 ± 0.38 (5)	2.10 ± 0.32	1.4 ± 0.2 × 10 ⁻⁴	1.186 × 10 ⁻³
39.6	1.85 ± 0.30 (4)	1.57 ± 0.26	1.1 ± 0.2 × 10 ⁻⁴	1.045 × 10 ⁻³
44.0	2.05 ± 0.33 (2)	1.74 ± 0.30	1.2 ± 0.2 × 10 ⁻⁴	9.97 × 10 ⁻⁴

Brimblecombe (1990) have established specific Pitzer ion interaction parameters for oxygen dissolved in salt solutions and brines, from which oxygen activity coefficients are calculated using Equation (5). Specific Pitzer ion interaction parameters given by Clegg and Brimblecombe are given in Appendix B.

By substituting the ion-specific and gas-specific parameters given in Appendix A (Hermann, Dewes, and Schumpe 1995) into Equation (4), the ratio of oxygen solubility in pure water to that in the simulated waste SY1-SIM-93B was calculated. No information was available for the aluminate anion; an estimate of $0.100 \text{ m}^3/\text{kmol}$ was chosen for the aluminate anion, based on values given for similar anions. The quantity $\log(c_{\text{O}_2, \text{O}}/c_{\text{O}})$ was estimated to be 1.076 at 25°C , which is the Sechenov constant K of Equation (2) multiplied by the electrolyte concentration. The activity coefficient for oxygen dissolved in the simulant at 25°C is simply calculated from Equation (3): $10^{1.076} = 11.9$. A lower solubility of oxygen in the simulant SY1-SIM-93B is predicted by the Schumpe model than is observed experimentally. Experimentally determined oxygen solubilities in simulated waste, solubilities calculated from the Schumpe and Pitzer models, and literature results for oxygen equilibria in pure water are compared in Figure 3.1 and in Table 3.2. It is again noted, however, that the data given in

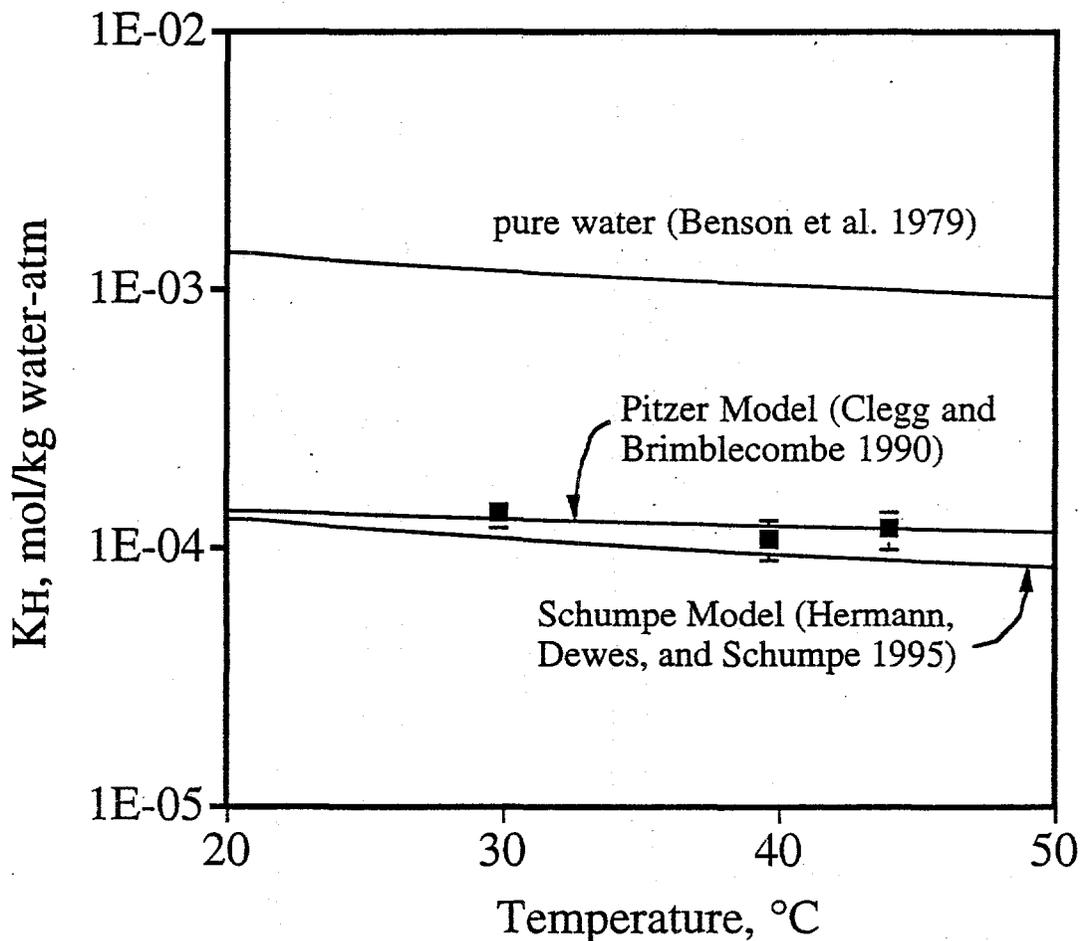


Figure 3.1. Experimental and Calculated Henry's Law Constants for Oxygen Dissolved in the Simulant SY1-SIM-93B

Table 3.2. Calculated and Measured Oxygen Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93\text{B})$	Schumpe Model*	Pitzer Model**
20.0			9.9
25.0		10.9	9.5
29.8	8.5 ± 1.2		9.1
30.0			9.1
35.0			8.8
39.6	9.5 ± 1.7		8.5
40.0			8.5
44.0	8.3 ± 1.4		8.3
45.0			8.3
50.0			8.1
*Calculated from Hermann, Dewes, and Schumpe (1995).			
**Calculated from Clegg and Brimblecombe (1990).			

Appendix A are strictly valid only at 25°C (298.2 K) and no temperature dependencies were given for the parameters h_{ion} and h_g . Schumpe (1993) has estimated that similar calculations should be valid at $298 \pm 5\text{K}$, since the temperature dependence of the interaction parameters are generally quite small.

Oxygen solubilities calculated using the Pitzer ion interaction model (Equation [4]) and the parameters given in Appendix B (Clegg and Brimblecombe 1990) were in good agreement with solubilities determined experimentally. Solubilities calculated using the Pitzer ion interaction model are included in Figure 3.1 and in Table 3.2. Oxygen-ion interaction parameters $\lambda_{O_2,c}$ and $\lambda_{O_2,a}$ (for cations and anions, respectively) and oxygen-neutral salt interaction parameters $\zeta_{O_2,ca}$ were used in the calculations. No information on salt-salt interaction parameters was available. Estimates were made for both the aluminate and nitrite ions, since neither were included in the data of Clegg and Brimblecombe (1990). In these calculations, aluminate ions were assumed to behave identically to hydroxide ions, and nitrite ions were assumed to behave identically to nitrate ions. Unlike the Schumpe model parameters given in Appendix A, the temperature dependence of many of the Pitzer interaction parameters has been given, and are included in Appendix B.

3.2 Hydrogen

Hydrogen solubilities in the homogeneous simulant SY1-SIM-93B were determined at three temperatures, given in Table 3.3. The number enclosed by parentheses in the second column of Table 3.3 indicates the number of determinations made at that temperature. As discussed in Section 3.1 for oxygen, uncertainties represent one standard deviation. Where only two determinations were made for a particular temperature, the standard deviation was estimated based on data obtained at

Table 3.3. Hydrogen Solubility in Simulant SY1-SIM-93B

Temperature, °C	Volume Dissolved per Liter Simulant (STP)	Volume Dissolved per kg Simulant (STP)	Henry's Law Constant, mole/kg water-atm	Henry's Law Constant for Pure Water, mole/kg water-atm
29.8	2.87 ± 0.47 (4)	2.43 ± 0.40	1.6 ± 0.3 × 10 ⁻⁴	7.66 × 10 ⁻⁴
39.6	2.30 ± 0.38 (4)	1.95 ± 0.32	1.3 ± 0.2 × 10 ⁻⁴	7.39 × 10 ⁻⁴
44.0	2.35 ± 0.40 (2)	2.00 ± 0.34	1.3 ± 0.2 × 10 ⁻⁴	7.32 × 10 ⁻⁴

other temperatures. Hydrogen solubilities were suppressed in the simulant when compared to literature values for pure water to an extent similar to the behavior of oxygen.

The solubility of hydrogen in pure water has been summarized by Young (1981a) from an extensive survey of existing data. For a hydrogen partial pressure of 1 atm, the mole fraction solubility X_{hydrogen} is:

$$\ln X_{\text{hydrogen}} = -125.939 + 5528.45/T(\text{K}) + 16.8893 \ln [T(\text{K})] \quad (8)$$

or

$$\ln K_{\text{H,hydrogen}} [\text{mole/kg water-atm}] = -121.922 + 5528.45/T(\text{K}) + 16.8893 \ln [T(\text{K})] \quad (9)$$

Data on the solubility of hydrogen in electrolyte solutions are largely limited to sodium chloride brines. Young (1981a) reviewed hydrogen solubility data in sodium chloride solutions given by Morrison and Billet (1952) and by Crozier and Yamamoto (1974). At 25°C, hydrogen was approximately a factor of three less soluble in 5 N sodium chloride solutions than in pure water. Hermann, Dewes, and Schumpe (1995) utilized the data of Clever (1983) in deriving a gas-specific parameter h_G value of -0.0176 m³/kmol for hydrogen. Detailed specific Pitzer ion interaction parameters for hydrogen in mixed electrolyte solutions, including a temperature dependence such as those given for oxygen in Appendix B, were not available.

Hydrogen solubilities in the simulant SY1-SIM-93B may be estimated from Equation (4) and the data given in Table 2.1 and Appendix A. A value for γ_i of 6.72 is obtained for hydrogen dissolved in this simulant mixture following the Schumpe model. This estimation is considered valid at $\approx 25 \pm 5^\circ\text{C}$ (Schumpe 1993). Calculated and experimentally determined Henry's Law constants are compared in Figure 3.2 and in Table 3.4. The Schumpe model would appear to slightly underestimate the solubility of hydrogen in this simulant, yielding values 1 or more standard deviations smaller than the experimentally determined values.

Hydrogen solubilities in Hanford Site waste mixtures can also be estimated using the approach given by Pasamehmetoglu et al. (1994), where gas interaction parameters given in Table 1.1 are substituted into Equation (6). In this approach, a hypothetical average salt was defined by averaging the salt-salt interaction parameter $\beta_{1,ss}$ for approximately sixty 1-1 electrolytes, from which a value of 0.17 at

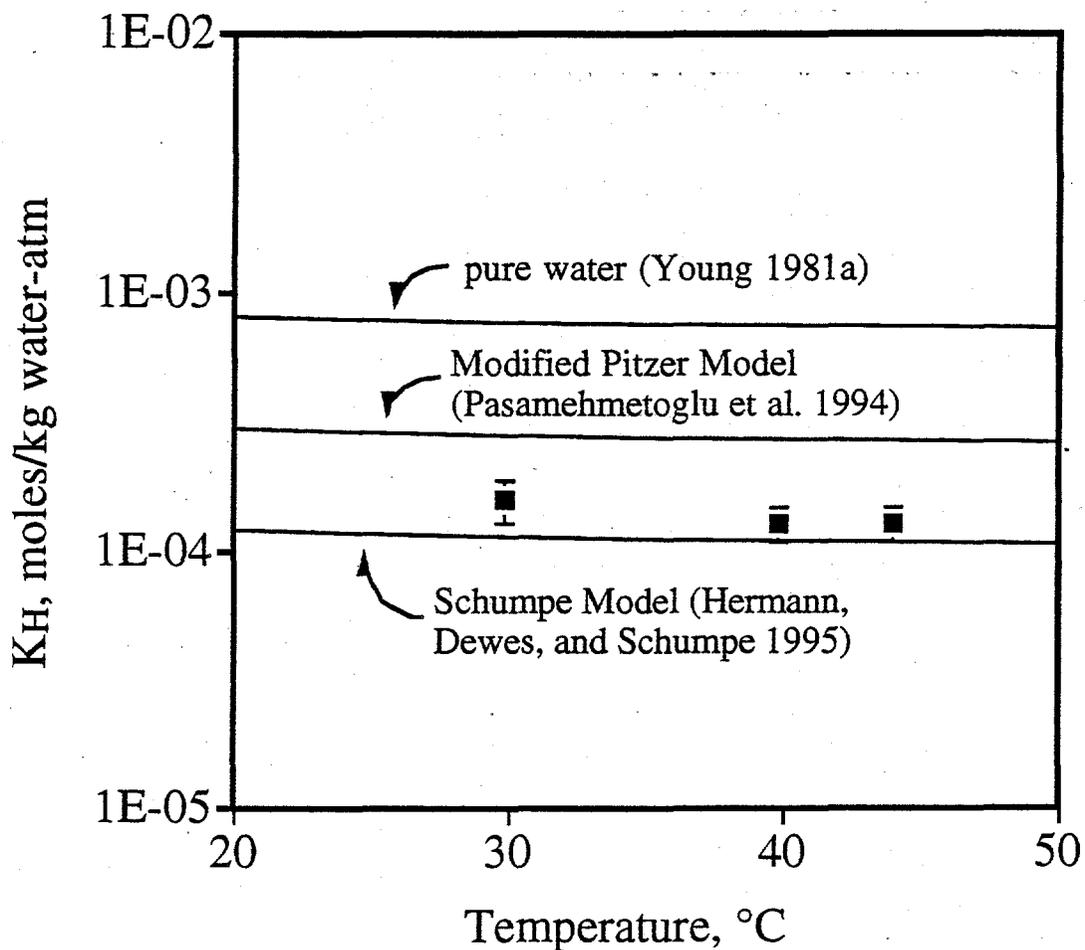


Figure 3.2. Experimental and Calculated Henry's Law Constants for Hydrogen Dissolved in the Simulant SY1-SIM-93B. Calculated results are based on 25°C data.

Table 3.4. Calculated and Measured Hydrogen Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93\text{B})$	Schumpe Model*	Pasamehmetoglu et al. (1994) Model
25.0		6.72	2.73
29.8	4.9 ± 0.9		
39.6	5.7 ± 0.9		
44.0	5.6 ± 0.9		

*Calculated from Hermann, Dewes, and Schumpe (1995).

25°C was obtained. This particular parameter is independent of the gas species. For the simulant SY1-SIM-93B, the total salt concentration per kilogram of water is 7.4 molal, as given in Table 2.1. Substituting the salt concentration and gas interaction parameters of Table 1.1 into Equation (6), a value of 2.73 was calculated for γ_i . Although expected to be small, no temperature dependence of the gas interaction parameters were provided by Pasamehmetoglu et al. (1994). As given in Figure 3.2 and Table 3.4, this model leads to predicted solubilities considerably higher than was observed experimentally. Of the two models and chosen interaction parameters, clearly the Schumpe model provides better agreement with experimental data.

3.3 Nitrogen

Nitrogen solubilities were determined at three temperatures in the homogeneous simulant SY1-SIM-93B, as given in Table 3.5. Again, the number enclosed by parentheses in the second column of Table 3.5 indicates the number of determinations made at that temperature. Uncertainties represent one standard deviation; where only two determinations were made for a particular temperature, the standard deviation was estimated based on data obtained at other temperatures. Nitrogen solubilities were lowered by the presence of dissolved electrolytes, in a manner very similar to the behavior of oxygen and hydrogen, and following general trends predicted by the Sechenov equation. Within experimental error, there was no obvious trend in the measured solubility as a function of temperature.

Nitrogen solubility data in pure water has been evaluated by Battino (1982). For a nitrogen partial pressure of 1 atm, the mole fraction solubility X_{nitrogen} is:

$$\ln X_{\text{nitrogen}} = -125.939 + 8632.13/T(K) + 24.7981 \ln [T(K)] \quad (10)$$

or

$$\ln K_{H,\text{nitrogen}} [\text{mole/kg water-atm}] = -121.922 + 8632.13/T(K) + 24.7981 \ln [T(K)] \quad (11)$$

Table 3.5. Nitrogen Solubility in Simulant SY1-SIM-93B

Temperature, °C	Volume Dissolved per Liter Simulant (STP)	Volume Dissolved per kg Simulant (STP)	Henry's Law Constant, mole/kg water-atm	Henry's Law Constant for Pure Water, mole/kg water-atm	$\frac{K_{H(93B)}}{K_{H(\text{water})}}$
29.8	1.05 ± 0.20 (2)	0.89 ± 0.17	6.0 ± 1.2 × 10 ⁻⁵	6.17 × 10 ⁻⁴	9.7 ± 1.9 × 10 ⁻²
39.6	0.72 ± 0.12 (3)	0.61 ± 0.10	4.1 ± 0.7 × 10 ⁻⁵	5.55 × 10 ⁻⁴	7.4 ± 1.3 × 10 ⁻²
44.0	1.10 ± 0.20 (2)	0.93 ± 0.17	6.2 ± 1.2 × 10 ⁻⁵	5.33 × 10 ⁻⁴	1.2 ± .2 × 10 ⁻¹

Nitrogen solubility behavior has been studied extensively in sodium chloride solutions, as reviewed by Battino (1982). The solubility of nitrogen has been found to be approximately 5 times less in 5 N sodium chloride solution than in pure water at 25°C, similar to the behavior of hydrogen and oxygen. There is little temperature dependence of nitrogen solubility in concentrated sodium chloride solutions (>5 N) (Battino 1982). Hermann, Dewes, and Schumpe (1995) derived a gas-specific parameter h_G for nitrogen (0.0002 m³/kg) virtually identical to that of oxygen (0.0000 m³/kg, see Appendix A), indicating that the solubilities of the two gases in electrolyte solutions should be affected in the same manner. Detailed specific Pitzer ion interaction parameters for nitrogen in mixed electrolyte solutions, such as those given for oxygen in Appendix B, were not found.

Nitrogen solubilities in the simulant SY1-SIM-93B can be estimated using Equation (4) and the data of Table 2.1 and Appendix A. A value for γ_i of 10.93 is obtained, indicating that a relatively strong salting-out effect is expected. Again, no temperature dependence of the ion-specific and gas-specific parameters were given by Hermann, Dewes, and Schumpe (1995); estimations of γ_i are expected to be valid at 25 ± 5°C. Calculated and observed Henry's Law constants are compared in Figure 3.3, while

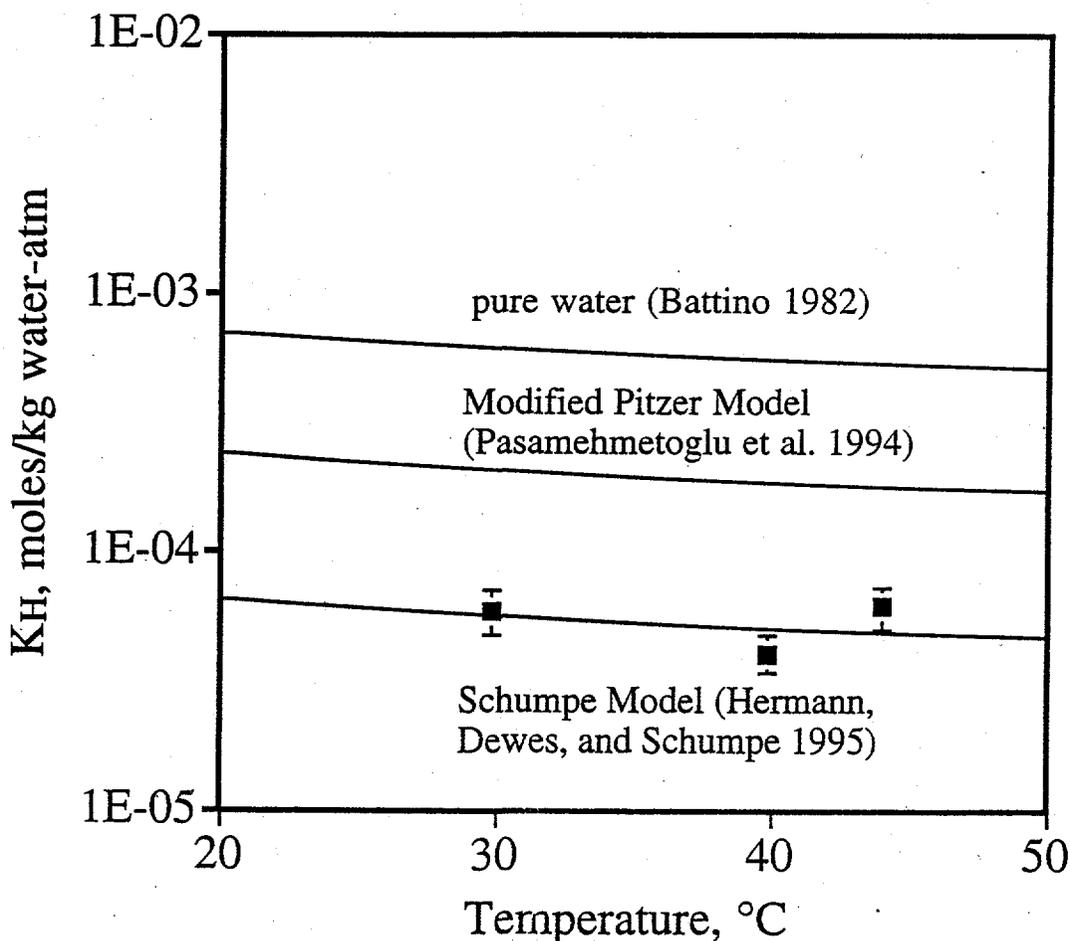


Figure 3.3. Experimental and Calculated Henry's Law Constants for Nitrogen Dissolved in the Simulant SY1-SIM-93B. Calculated results are based on 25°C data.

a comparison of experimentally observed and calculated values of γ_i are given in Table 3.6. Experimental Henry's Law constants agreed with those calculated using the Schumpe model to nearly within one standard deviation of the experimental data.

Predicted Henry's Law constants for nitrogen solubilities in the simulant SY1-SIM-93B using Equation (6) are readily calculated using the parameters given in Table 2.1, the total salt concentration per kilogram water of 7.4 molal (see Table 2.1), and a value for the salt-salt interaction parameter $\beta_{1,ss}$ of 0.17. A value for γ_i of 2.73 is obtained, identical to that for hydrogen for this simulant at 25°C. Again, assuming that the temperature dependence of specific interaction parameters is small, estimates are also made for temperatures greater than 25°C, following Pasamehmetoglu et al. (1994). This method predicts solubilities considerably higher than are observed experimentally (see Figure 3.3 and Table 3.6).

3.4 Methane

Methane solubilities in the simulant SY1-SIM-93B were determined at three temperatures, as given in Table 3.7. The number enclosed by parentheses in the second column of Table 3.7 has the same meaning as before; uncertainties were determined as described above. Methane solubilities exhibited the familiar salting-out effect, in a manner very similar to the behavior of oxygen and nitrogen, and as predicted by the Sechenov equation.

Table 3.6. Calculated and Measured Nitrogen Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93\text{B})$	Schumpe Model*	Pasamehmetoglu et al. (1994) Model
25.0		10.93	2.73
29.8	10.3 ± 2.1		
39.6	13.5 ± 2.3		
44.0	8.6 ± 1.9		

*Calculated from Hermann, Dewes, and Schumpe (1995), valid at 25°C.

Table 3.7. Methane Solubility in Simulant SY1-SIM-93B

Temperature, °C	Volume Dissolved per Liter Simulant (STP)	Volume Dissolved per kg Simulant (STP)	Henry's Law Constant, mole/kg water-atm	Henry's Law Constant for Pure Water, mole/kg water-atm
29.8	1.50 ± 0.25 (4)	1.27 ± 0.21	$8.5 \pm 1.4 \times 10^{-5}$	1.319×10^{-3}
39.6	1.69 ± 0.14 (2)	1.43 ± 0.24	$9.6 \pm 1.6 \times 10^{-5}$	1.148×10^{-3}
44.0	1.29 ± 0.22 (2)	1.09 ± 0.18	$7.3 \pm 1.2 \times 10^{-5}$	1.095×10^{-3}

Data on the solubility of methane in pure water has been evaluated by Clever and Young (1987) and by Rettich et al. (1981). Methane is approximately two times more soluble in pure water than either hydrogen or nitrogen. For a methane partial pressure of 1 atm, the mole fraction solubility X_{methane} is (Clever and Young 1987):

$$\ln X_{\text{methane}} = -416.1595 + 15557.56/T(\text{K}) + 65.2553 \ln [T(\text{K})] - 616.70 T(\text{K}) \quad (12)$$

or

$$\ln \cdot K_{\text{H,methane}} [\text{mole/kg water-atm}] = -411.2142 + 15557.56/T(\text{K}) + 65.2553 \ln [T(\text{K})] - 616.70 T(\text{K}) \quad (13)$$

The last term of Equation (12) was given in the Handbook of Chemistry and Physics 74th Ed. (1993) as $-6.6170 T^*$, where $T^* = T(\text{K})/100$. This term is assumed to be in error, since the expression does not agree with the original literature.

Methane solubility behavior has been most extensively studied in sodium chloride solutions, as reviewed by Clever and Young (1987). In 5 N sodium chloride solutions, methane is approximately 5 times less soluble than in pure water at 25°C, similar to the behavior of hydrogen and oxygen. Hermann, Dewes, and Schumpe (1995) derived the positive gas-specific parameter h_g for methane of 0.0028 m³/kmol (see Appendix A), indicating that a larger salting-out effect should be observed for methane than for many gases such as nitrous oxide, nitrogen, oxygen, ammonia, and hydrogen. Detailed specific Pitzer ion interaction parameters for methane in mixed electrolyte solutions, including a temperature dependence such as those given for oxygen in Appendix B, were not available.

Methane solubilities in the simulant SY1-SIM-93B can be estimated using Equation (4) (Schumpe model) and the data of Table 2.1 and Appendix A. A value for γ_i of 11.74 is obtained, indicating that a relatively strong salting-out effect is expected. Again, no temperature dependence of the ion-specific and gas-specific parameters were given by Hermann, Dewes, and Schumpe (1995). Schumpe (1993) reports that the valid temperature range should be $\pm 5\text{K}$ due to the small temperature dependence of specific interaction parameters. Calculated and observed Henry's Law constants are compared in Figure 3.4, while a comparison of experimentally observed and calculated values of γ_i are given in Table 3.8. Calculated and experimentally determined Henry's Law constants agreed to within less than two standard deviations of the experimental data.

3.5 Nitrous Oxide

Nitrous oxide solubilities in the simulant SY1-SIM-93B were determined at three temperatures, as given in Table 3.9. The number enclosed by parentheses in the second column of Table 3.9 and uncertainties have the same meaning as before. Nitrous oxide is by far the most soluble in water and electrolyte solutions of the series of gases considered in this study. Reduced sample volumes were necessary to keep the volume of gas dissolved within the range of the gas burets (approximately 100 mL samples were used in nitrous oxide solubility measurements, whereas approximately 300 mL samples were used in solubility measurements involving oxygen, nitrogen, methane, and hydrogen).

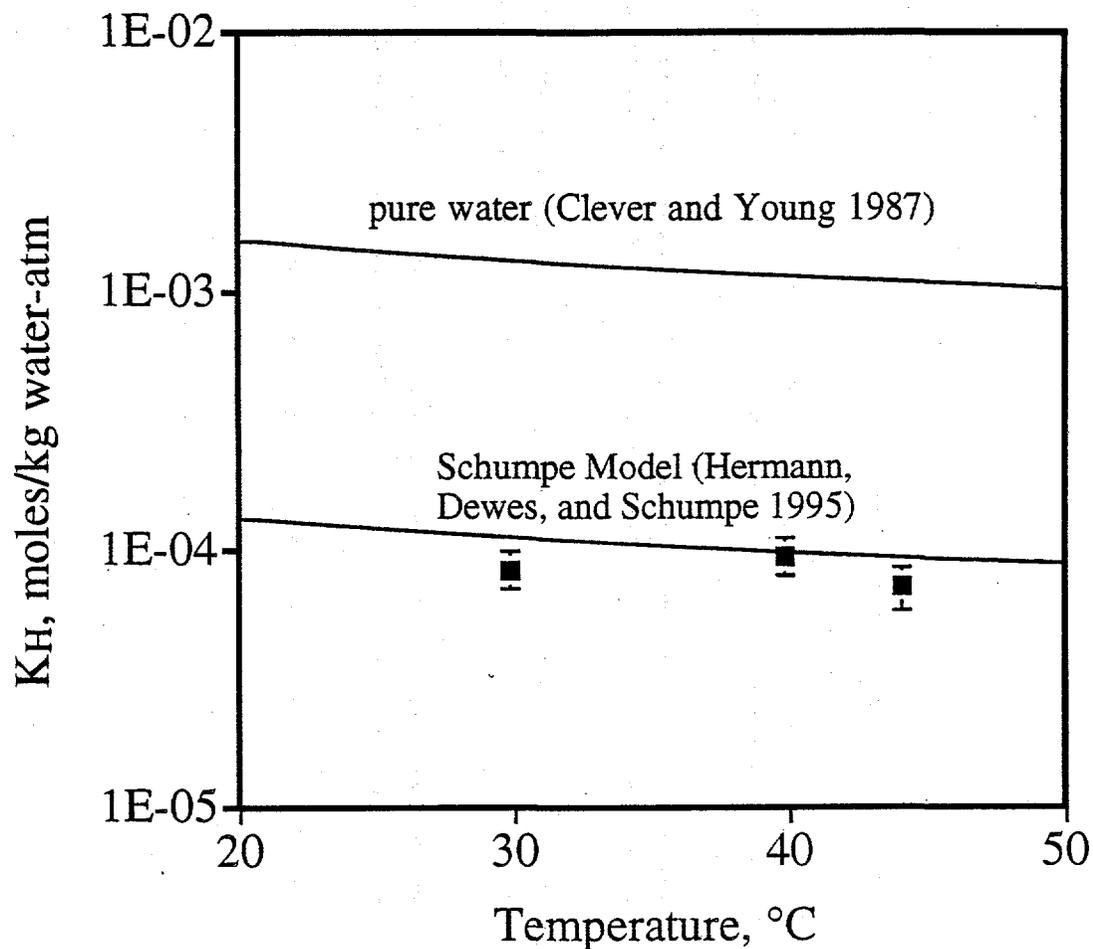


Figure 3.4. Experimental and Calculated Henry's Law Constants for Methane Dissolved in the Simulant SY1-SIM-93B. Calculated results are based on 25°C data.

Table 3.8. Calculated and Measured Methane Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93B)$	Schumpe Model*
25.0		11.74
29.8	15.5 ± 2.6	
39.6	12.0 ± 2.1	
44.0	15.0 ± 2.6	
*Calculated from Hermann, Dewes, and Schumpe (1995).		

Table 3.9. Nitrous Oxide Solubility in Simulant SY1-SIM-93B

Temperature, °C	Volume Dissolved per Liter Simulant (STP)	Volume Dissolved per kg Simulant (STP)	Henry's Law Constant, mole/kg water-atm	Henry's Law Constant for Pure Water, mole/kg water-atm
29.8	54.7 ± 8.2 (3)	46.4 ± 7.0	3.1 ± 0.5 × 10 ⁻³	2.12 × 10 ⁻²
39.6	48.2 ± 9.6 (3)	40.8 ± 8.2	2.7 ± 0.5 × 10 ⁻³	1.66 × 10 ⁻²
44.0	42.9 ± 8.6 (2)	36.4 ± 7.3	2.4 ± 0.5 × 10 ⁻³	1.51 × 10 ⁻²

The solubility of nitrous oxide was lowered by the presence of dissolved electrolytes. The magnitude of the salting-out effect was among the smallest of the gases studied, however.

Young (1981b) has evaluated data on the solubility of nitrous oxide in pure water. Nitrous oxide is approximately two orders of magnitude more soluble in pure water than other gases considered in this study. For a nitrous oxide partial pressure of 1 atm, the mole fraction solubility $X_{\text{nitrous oxide}}$ is:

$$\ln X_{\text{nitrous oxide}} = -158.6208 + 8882.80/T(K) + 21.2531 \ln [T(K)] \quad (14)$$

or

$$\ln K_{H,\text{nitrous oxide}} [\text{mole/kg water-atm}] = -154.6035 + 8882.80/T(K) + 21.2531 \ln [T(K)] \quad (15)$$

Nitrous oxide solubility behavior in electrolyte solutions has been reviewed by Young (1981b). Information on the solubility of nitrous oxide in sodium nitrate solutions up to approximately 5 molal at temperatures from 20 to 25°C was provided in this review. The solubility of nitrous oxide was lowered by a factor of ≈ 2.5 in 5 molal sodium nitrate compared to that in pure water. Detailed specific Pitzer ion interaction parameters for nitrogen in mixed electrolyte solutions are not available, nor is information on the temperature dependence of nitrous oxide solubility. Hermann, Dewes, and Schumpe (1995) derived a value of $-0.0110 \text{ m}^3/\text{kmole}$ for gas-specific parameter h_g for nitrous oxide (see Appendix A), indicating a somewhat smaller salting-out effect should be seen for this gas than for oxygen ($0.0000 \text{ m}^3/\text{kmole}$) or nitrogen ($0.0002 \text{ m}^3/\text{kmole}$), for example. High positive values for h_g indicate a relatively large salting-out effect; high negative values indicate a small salting-out effect in the Schumpe model.

Nitrous oxide solubilities in the simulant SY1-SIM-93B can be estimated using Equation (4) and the data of Table 2.1 and Appendix A. A value for γ_i of 8.28 is obtained for nitrous oxide dissolved in this simulant. No temperature dependence of these or any other ion-specific and gas-specific parameters were given by Hermann, Dewes, and Schumpe (1995), so extrapolation to temperatures other than 25°C should be done with caution. Calculated and observed Henry's Law constants are compared in Figure 3.5, while a comparison of experimentally observed and calculated values of γ_i are given in Table 3.10. The Schumpe model gave estimated Henry's Law constants somewhat smaller than obtained experimentally, but within approximately 1 standard deviation. Experimentally determined Henry's Law constants were consistently smaller than those calculated following Pasamehmetoglu et al. (1994) by a factor of 2 to 3.

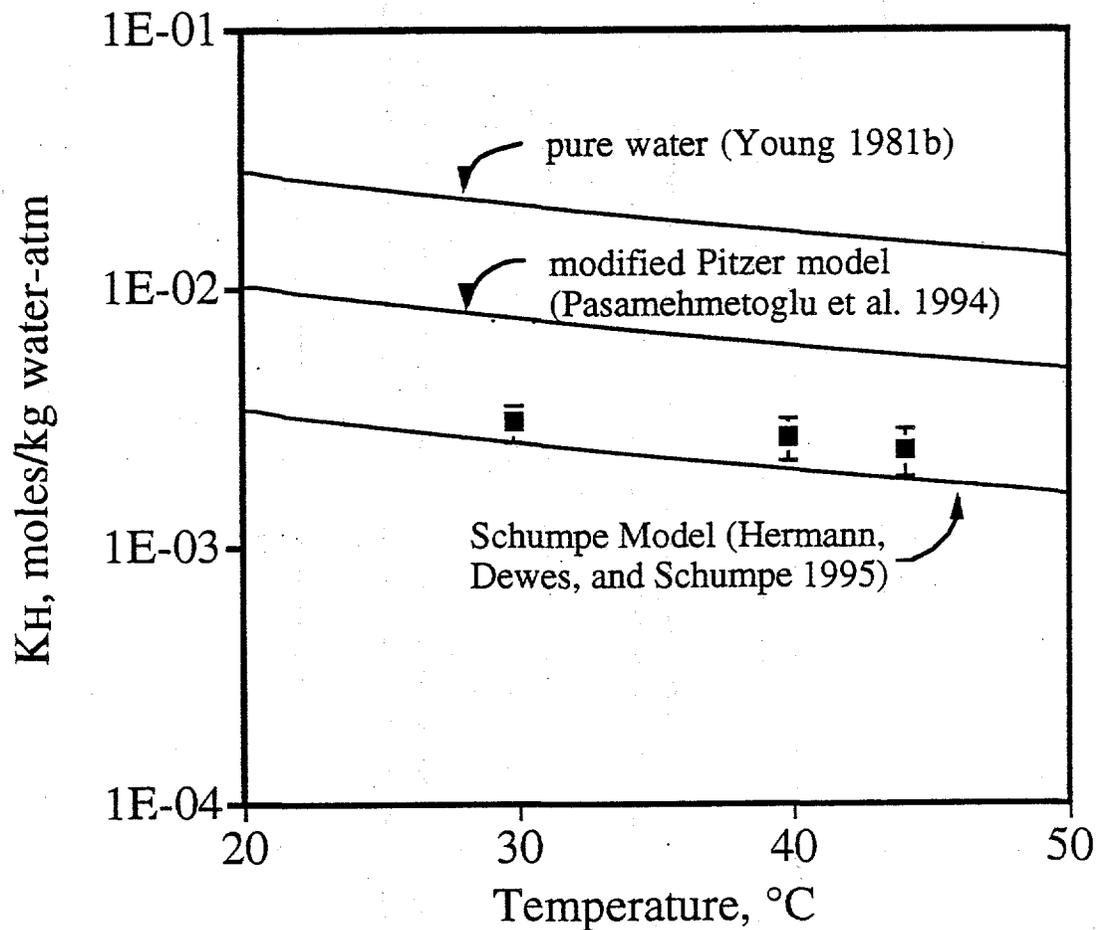


Figure 3.5. Experimental and Calculated Henry's Law Constants for Nitrous Oxide Dissolved in the Simulant SY1-SIM-93B. Calculated results are based on 25°C data.

Table 3.10. Calculated and Measured Nitrous Oxide Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93\text{B})$	Schumpe Model*	Pasamehmetoglu et al. (1994) Model
25.0		8.28	2.75
29.8	6.8 ± 1.2		
39.6	6.1 ± 1.0		
44.0	6.3 ± 1.1		

*Calculated from Hermann, Dewes, and Schumpe (1995).

3.6 Ammonia

Ammonia solubilities in pure water and in electrolyte solutions have been reviewed in detail by Clegg and Brimblecombe (1989). In pure water, Henry's Law constants for ammonia may be calculated from the expression:

$$\ln K^{H,\text{ammonia}} [\text{mole/kg water-atm}] = -8.0964 + 3917.50/T - 0.00314T \quad (16)$$

Pitzer ion interaction terms were derived by Clegg and Brimblecombe (1989) from a survey of literature data for a wide range of electrolytes.

Ammonia solubilities in the simulant SY1-SIM-93B, in the simulant SY1-SIM-91A, and in sodium hydroxide solutions have been reported by Norton and Pederson (1994). Henry's Law constants corresponding to approximately 0.6 weight % ammonia in the simulant as a function of temperature are reproduced in Table 3.11, in addition to Henry's Law constants for ammonia in pure water (Clegg and Brimblecombe 1989). While the familiar salting-out behavior is apparent for ammonia in concentrated electrolytes, the magnitude of lowering of solubility due to the presence of dissolved electrolytes was smaller than that observed for oxygen, nitrogen, nitrous oxide, hydrogen, or methane. Ammonia remains highly soluble in the simulant, approximately four orders of magnitude more soluble than nitrous oxide, for example.

Table 3.11. Ammonia Solubility in Simulant SY1-SIM-93B and in Pure Water

Temperature, °C	Henry's Law Constant for the Simulant SY1-SIM-93B,* mole/kg water-atm	Henry's Law Constant for Pure Water,** mole/kg water-atm
27.6	22.3	53.8
32.2	18.3	43.5
37.3	15.1	34.7
43.1	12.1	27.0
48.9	9.8	21.2
55.3	7.8	16.4
60.8	6.6	13.3
65.5	5.7	11.1
70.9	4.9	9.1

* Norton and Pederson (1994)
 **Clegg and Brimblecombe (1989)

Experimentally determined ammonia solubilities in the simulant SY1-SIM-93B (Norton and Pederson 1994) are in relatively good agreement with predicted solubilities following the Schumpe model (Hermann, Dewes, and Schumpe 1995), the Pitzer ion interaction model (Clegg and Brimblecombe 1989), and the modified Pitzer model (Pasamehmetoglu et al. 1994). Experimental data and predicted solubilities are compared in Figure 3.6 and in Table 3.12. Parameters used in calculations following the Pitzer model have been given previously by Norton and Pederson (1994). Those used in calculations following the Schumpe model are given in Appendix A, while parameters recommended by Pasamehmetoglu et al. (1994) are provided in Table 1.1. The three models predict nearly identical ammonia solubilities in the simulated waste. For all three models, interaction parameters were based primarily on data corresponding to 25°C. The temperature dependence of Henry's Law constants for the simulated waste shown in Figure 3.6 derives nearly completely from the temperature dependence for ammonia solubilities in pure water. Clearly, agreement between experimental results and predicted ammonia solubilities is best at ≈25°C, as expected. The three models tend to somewhat underpredict the solubility of ammonia in concentrated electrolyte solutions at higher temperatures.

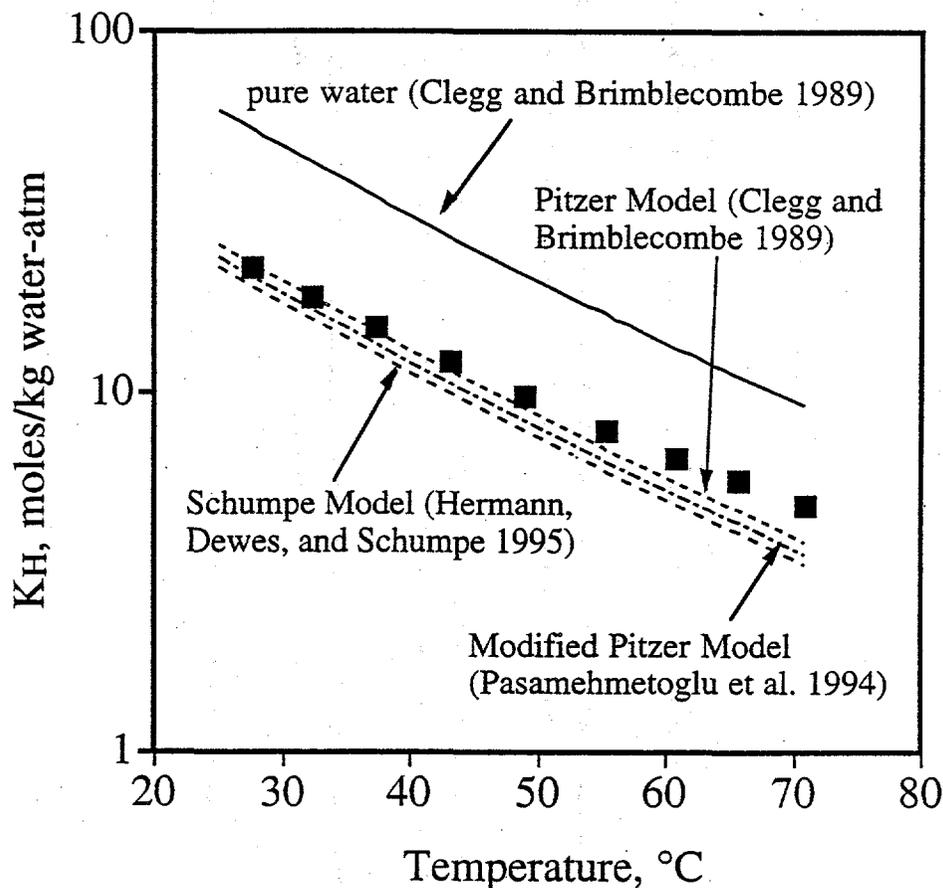


Figure 3.6. Experimental and Calculated Henry's Law Constants for Ammonia Dissolved in the Simulant SY1-SIM-93B. Calculated results are based on 25°C data.

Table 3.12. Calculated and Measured Ammonia Activity Coefficients for Simulant SY1-SIM-93B

Temperature, °C	$K_H(\text{water})/K_H(93\text{B})^{(a)}$	Schumpe Model ^(b)	Pitzer Model ^(c)	Pasamehmetoglu Model ^(d)
25.0		2.73	2.37	2.57
27.6	2.41			
32.2	2.38			
37.3	2.30			
43.1	2.23			
48.9	2.17			
55.3	2.11			
60.8	2.01			
65.5	1.95			
70.9	1.86			

(a) Experimental data from Norton and Pederson (1994)
 (b) Calculated from Hermann, Dewes, and Schumpe (1995)
 (c) Calculated from Clegg and Brimblecombe (1989)
 (d) Calculated from Pasamehmetoglu et al. (1994)

4.0 Estimated Gas Solubilities in Hanford Wastes

The solubilities of the gases oxygen, nitrogen, hydrogen, methane, nitrous oxide, and ammonia in Hanford Site wastes may be estimated using data presented above and using existing models. Confidence in such estimates is bolstered by the reasonably good agreement obtained between laboratory data found in the present study for a simulated waste and gas solubilities calculated using existing models. Actual waste mixtures are considerably more concentrated than the simulant SY1-SIM-93B used in this study, so the extent of the salting-out effect in actual wastes should be considerably larger than observed in the simulant, as per the Sechenov equation (Sechenov 1889), the Schumpe model (Schumpe 1993; Hermann, Dewes, and Schumpe 1995), the Pitzer ion interaction model (Pitzer 1987; 1990), and modifications to the Pitzer model (Edwards et al. 1978; Pasamehmetoglu et al. 1994). That is, the solubility of gases in actual waste mixtures should be much smaller than found for pure water or for the simulated waste used here. Except for ammonia and, to a lesser extent nitrous oxide, the gases included in this study are all relatively non-polar, so similar trends in solubility versus electrolyte concentration are expected. Association between gas molecules, dipole-dipole, or dipole-ion interactions should not be important.

There are several caveats that should be considered when gas solubilities in Hanford Site wastes are predicted using existing models and the present data. The composition of the liquid phase is needed in modeling gas solubilities, not necessarily the overall waste composition that also includes considerable quantities of solid phases. The composition of various segments of the wastes in Tank 241-SY-101 have been given by Herting et al. (1992a). Reynolds (1992) has given a composition of the mother liquor from an analysis of this data, reproduced in Table 4.1. It is this waste composition on which

Table 4.1. Mother Liquor Composition of Tank 241-SY-101 (from Reynolds 1992)

Component	wt %	Molarity	Molality
H ₂ O	36.1	--	--
Na ⁺	20.0	12.7	24.10
OH ⁻	2.5	2.15	4.08
NO ₂ ⁻	12.1	3.85	7.30
NO ₃ ⁻	11.3	2.67	5.06
Al	3.21	1.74	3.30
Fe	0.0016	0.0004	0.00076
Cr	0.0068	0.0019	0.0036
Ca	0.0088	0.0032	0.00061
TOC	1.12	--	--
TIC	0.46	0.56	1.06
SpG	1.46	--	--

solubilities are estimated. Raising the temperature of the wastes also changes the composition of the liquid phase (Barney 1976; Reynolds and Herting 1984). Specific ion interaction terms have not yet been established for all of the components of the wastes, nor have the temperature dependence of specific interaction terms been well established in many cases. The extent of the salting-out effect tends to diminish as the temperature is raised, as found for ammonia dissolved in simple electrolyte solutions (Clegg and Brimblecombe 1989) and in simulated Hanford Site waste mixtures (Norton and Pederson 1994). By using interaction parameters valid at 25°C in modeling solubilities at higher temperatures, one would tend to underestimate gas solubilities in strong electrolyte solutions. Finally, there are no interaction parameters available for organic components of the wastes, although these are expected to be of relatively minor importance.

As discussed in the previous section, the Schumpe model gave solubility estimations in reasonably good agreement with experimentally determined gas solubilities in a simulated waste mixture. Such calculations may be extended to estimate the solubility of oxygen, nitrogen, hydrogen, methane, nitrous oxide, and ammonia in actual waste mixtures. Contributions of each ion to γ_i for the mother liquor of wastes in Tank 241-SY-101 calculated using the Schumpe model are given in Table 4.2. For each of the five gases considered in this study, the sodium ion contributed the most to the salting-out effect, followed by nitrite, hydroxide, and aluminate. Despite being a major component, the nitrate ion contributed little to reductions in gas solubility in the Schumpe model. Ammonia solubilities are predicted to be the least affected by the presence of electrolytes (solubility reduction by a factor of ≈ 9 compared to pure water at 25°C), while methane solubilities are predicted to be the most strongly affected (solubility reduction by a factor of 136 compared to pure water). These salting-out effects are

Table 4.2. Schumpe Model Estimation of γ_i for the Mother Liquor of Tank 241-SY-101*

Component	Oxygen ($h_{\text{ion}} + h_{\text{O}_2}$) c_{ion}	Nitrogen ($h_{\text{ion}} + h_{\text{N}_2}$) c_{ion}	Hydrogen ($h_{\text{ion}} + h_{\text{H}_2}$) c_{ion}	Methane ($h_{\text{ion}} + h_{\text{CH}_4}$) c_{ion}	Nitrous oxide ($h_{\text{ion}} + h_{\text{N}_2\text{O}}$) c_{ion}	Ammonia ($h_{\text{ion}} + h_{\text{NH}_3}$) c_{ion}
Na ⁺	1.37E+00	1.37E+00	1.15E+00	1.41E+00	1.24E+00	7.28E-01
OH ⁻	1.97E-01	1.98E-01	1.60E-01	2.03E-01	1.76E-01	8.86E-02
NO ₂ ⁻	2.80E-01	2.80E-01	2.12E-01	2.90E-01	2.41E-01	8.47E-02
NO ₃ ⁻	3.63E-02	3.68E-02	-1.07E-02	4.38E-02	9.61E-03	-9.88E-02
AlO ₂ ^{-**}	1.74E-01	1.74E-01	1.43E-01	1.79E-01	1.57E-01	8.60E-02
Fe ²⁺	6.78E-05	6.78E-05	6.07E-05	6.89E-05	6.38E-05	4.75E-05
Cr ³⁺	1.10E-04	1.10E-04	7.64E-05	1.15E-04	9.08E-05	1.37E-05
Ca ²⁺	4.94E-04	4.94E-04	4.37E-04	5.03E-04	4.62E-04	3.32E-04
CO ₃ ²⁻	8.72E-02	8.74E-02	7.74E-02	8.88E-02	8.17E-02	5.89E-02
total = log (γ_{gas})	2.145 (10 ^γ = 140)	2.150 (10 ^γ = 141)	1.729 (10 ^γ = 53.6)	2.212 (10 ^γ = 163)	1.909 (10 ^γ = 81.0)	0.947 (10 ^γ = 8.86)
*Interaction parameters from Schumpe (1993); Hermann, Dewes, and Schumpe (1995). The mother liquor composition is given in Table 4.1.						
**The interaction parameter h_i for the aluminate ion was estimated at 0.100 m ³ /kmol.						

approximately a factor of ten greater than determined experimentally for a much less concentrated but otherwise similar simulated waste mixture, SY1-SIM-93B. Estimated Henry's Law constants for the mother liquor are given in Table 4.3. These values were calculated using Equation (1) using γ_i values from Table 4.2 and using Henry's Law expressions for the solubility of each gas in pure water.

Henry's Law constants estimated using the Schumpe model for ammonia dissolved in mother liquor of Tank 241-SY-101 at $\approx 25^\circ\text{C}$ agreed quite well with experimentally determined Henry's Law constants for ammonia in the simulant SY1-SIM-91A, as shown in Figure 4.1. The deviation between calculated results for the mother liquor for Tank 241-SY-101 and measured results for the simulant SY1-SIM-91A grew larger with increases in temperature, however. Ammonia solubilities in this simulant were reported previously by Norton and Pederson (1994). The simulant SY1-SIM-91A is a heterogeneous slurry that is saturated with respect to sodium nitrate, sodium nitrite, sodium aluminate, and sodium carbonate at room temperature, the preparation of which has been described by Bryan and Pederson (1994). As such, this simulant may well provide a good match of the identity and concentration of the principal inorganic components of actual wastes at room temperature.

Assuming a negligible temperature dependence (no statistically valid trend could be seen in solubility results for any of the gases except for ammonia as a function of temperature), average gas activity coefficients γ_{gas} determined experimentally were calculated from all of the determinations for oxygen, hydrogen, nitrogen, methane, and nitrous oxide. Gas interaction parameters h_g given by Schumpe and co-workers (Schumpe 1993; Hermann, Dewes, and Schumpe 1995) were modified from those given in Appendix A to be consistent with experimental data for the simulant SY1-SIM-93B determined in this study. A summary of these original and modified interaction parameters are given in Table 4.4, while activity coefficient estimates for oxygen, nitrogen, hydrogen, methane, and nitrous oxide are given in Table 4.5.

Table 4.3. Henry's Law Constants for the Mother Liquor of Tank 241-SY-101
Calculated Using the Schumpe Model*

Temperature, $^\circ\text{C}$	$K_{H^{**}}$ oxygen	K_H nitrogen	K_H hydrogen	K_H methane	K_H nitrous oxide	K_H ammonia
20	9.96E-06	5.01E-06	1.51E-05	9.65E-06	3.47E-04	8.71
25	9.14E-06	4.65E-06	1.46E-05	8.78E-06	2.99E-04	6.85
30	8.46E-06	4.36E-06	1.43E-05	8.08E-06	2.61E-04	5.43
35	7.91E-06	4.12E-06	1.40E-05	7.50E-06	2.30E-04	4.34
40	7.44E-06	3.92E-06	1.38E-05	7.04E-06	2.04E-04	3.48
45	7.06E-06	3.77E-06	1.37E-05	6.66E-06	1.83E-04	2.82
50	6.74E-06	3.64E-06	1.36E-05	6.35E-06	1.65E-04	2.29
55	6.48E-06	3.55E-06	1.36E-05	6.10E-06	1.51E-04	1.88
60	6.26E-06	3.48E-06	1.36E-05	5.90E-06	1.38E-04	1.54

*Calculated using activity coefficients given in Table 4.2.
**Units of K_H are mole/kg $\text{H}_2\text{O-atm}$.

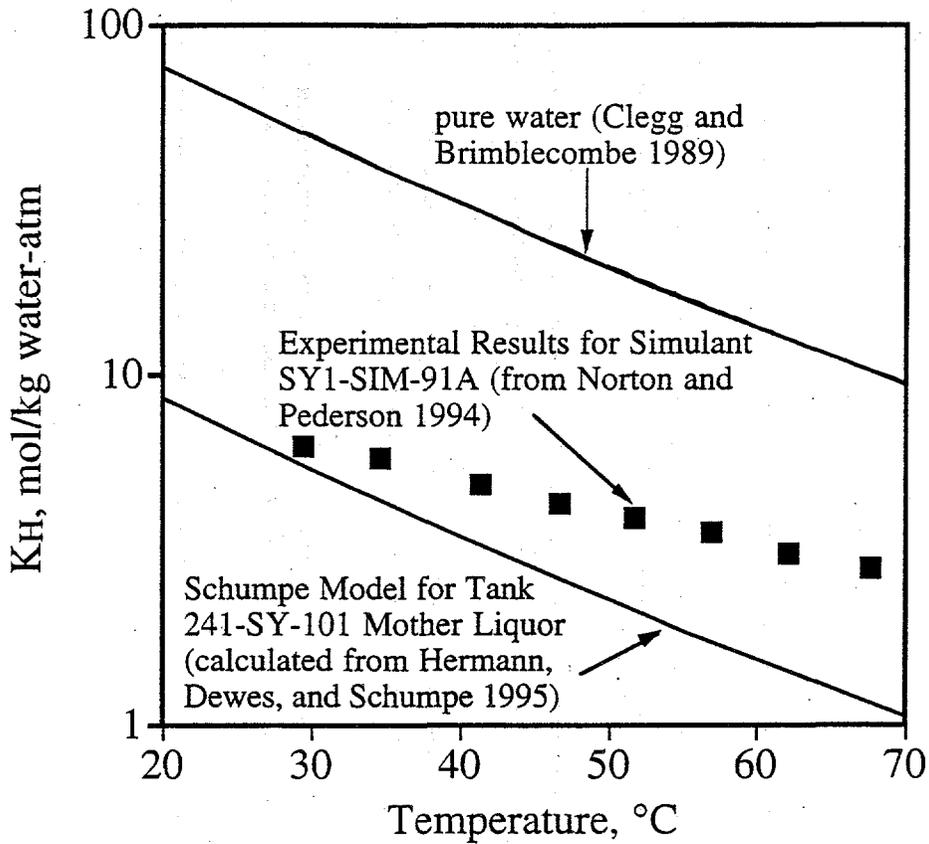


Figure 4.1. Comparison of Experimentally Determined Henry's Law Constants for the Simulant SY1-SIM-91A with Calculated Results Using the Schumpe Model for the Mother Liquor of Tank 241-SY-101.

Table 4.4. Gas Interaction Parameter Set h_g Consistent with Experimental Results

Gas	γ_i for 93B from Schumpe Model with original h_g values	γ_i for 93B observed experimentally [(x) = number of determinations]	Interaction parameters h_g given by Hermann, Dewes, and Schumpe (1995)	Required interaction parameters h_g to match experimental γ_i values for 93B
oxygen	10.87	8.8 ± 1.6 (11)	0.0000	-0.0078
nitrogen	10.93	11.2 ± 2.5 (7)	0.0002	0.0010
hydrogen	6.72	5.4 ± 1.0 (8)	-0.0176	-0.0255
methane	11.74	14.5 ± 2.6 (8)	0.0028	0.0105
nitrous oxide	8.28	6.4 ± 1.3 (8)	-0.0110	-0.0195

Table 4.5. Schumpe Model Estimation of γ_i for the Mother Liquor of Tank 241-SY-101 Using Modified Gas Interaction Constants*

Component	Oxygen ($h_{\text{ion}} + h_{\text{O}_2}$) c_{ion}	Nitrogen ($h_{\text{ion}} + h_{\text{N}_2}$) c_{ion}	Hydrogen ($h_{\text{ion}} + h_{\text{H}_2}$) c_{ion}	Methane ($h_{\text{ion}} + h_{\text{CH}_4}$) c_{ion}	Nitrous oxide ($h_{\text{ion}} + h_{\text{N}_2\text{O}}$) c_{ion}
Na ⁺	1.27E+00	1.38E+00	1.05E+00	1.50E+00	1.12E+00
OH ⁻	1.81E-01	2.00E-01	1.43E-01	2.20E-01	1.55E-01
NO ₂ ⁻	2.49E-01	2.83E-01	1.81E-01	3.20E-01	2.04E-01
NO ₃ ⁻	1.55E-02	3.90E-02	-3.18E-02	6.43E-02	-1.58E-02
AlO ₂ ^{-**}	1.60E-01	1.76E-01	1.30E-01	1.92E-01	1.40E-01
Fe ²⁺	6.46E-05	6.82E-05	5.76E-05	7.20E-05	6.00E-05
Cr ³⁺	9.50E-05	1.12E-04	6.14E-05	1.30E-04	7.28E-05
Ca ²⁺	4.69E-04	4.97E-04	4.12E-04	5.27E-04	4.31E-04
CO ₃ ²⁻	8.29E-02	8.78E-02	7.30E-02	9.31E-02	7.63E-02
total = log (γ_{gas})	1.961 (10 ^{γ} = 91.4)	2.169 (10 ^{γ} = 148)	1.542 (10 ^{γ} = 34.8)	2.394 (10 ^{γ} = 248)	1.684 (10 ^{γ} = 48.3)

*Modified gas interaction constants are given in Table 4.4.

The ammonia solubility data of Norton and Pederson (1994) for the simulant SY1-SIM-93B (see Figure 3.6) can be used to calculate modified Schumpe model interaction parameters that includes a temperature dependence. This is accomplished by adjusting only the value of h_{NH_3} from that given by Hermann, Dewes, and Schumpe (1995) ($h_{\text{NH}_3} = -0.0507 \text{ m}^3/\text{kmole}$; see Appendix A) to match experimentally determined activity coefficients γ_{NH_3} for the simulated waste as a function of temperature. Interaction parameters for each of the ions in this calculation are not adjusted in this calculation. Required values of h_{NH_3} are given in Table 4.6 and in Figure 4.2. A second order polynomial was fit to h_{NH_3} as a function of temperature (K), included in Figure 4.2.

Using these modified gas interaction parameters, Henry's Law constants are re-estimated for the mother liquor in Tank 241-SY-101, as given in Table 4.7. Predicted solubilities are higher by less than a factor of two when using the modified gas interaction parameters of Table 4.4 compared to those calculated using the interaction parameters given by Schumpe and coworkers. This is an almost insignificant change, considering the very small absolute magnitude of the gas solubilities and the extent of extrapolation of the Schumpe model to highly concentrated electrolyte solutions, for which no experimental gas solubility data are available.

The solubility of nitrogen, hydrogen, nitrous oxide, and ammonia in Hanford Site waste mixtures have been estimated by Pasamehmetoglu et al. (1994) using Equation (6) and the gas interaction parameters given in Table 1.1. An average value of 0.17 at 25°C for the salt-salt interaction parameter $\beta_{1,ss}$ was determined for the electrolytes present in Hanford Site tank wastes. As was the situation for parameters given by Schumpe and coworkers, no temperature dependence was given by Pasamehmetoglu et al. (1994) for any of the gas interaction parameters. Estimated Henry's Law

Table 4.6. Schumpe Model Gas Interaction Parameters h_{NH_3} for Ammonia in the Simulant SY1-SIM-93B Consistent with Experimental Results of Norton and Pederson (1994)

Temperature, °C	Experimentally determined ammonia activity coefficient γ_{NH_3} from Norton and Pederson (1994)	Required Schumpe Model interaction parameter for ammonia h_{NH_3} [m ³ /kmole]
27.6	2.41	-0.0551
32.2	2.38	-0.0556
37.3	2.30	-0.0569
43.1	2.23	-0.0580
48.9	2.17	-0.0590
55.3	2.11	-0.0601
60.8	2.01	-0.0618
65.5	1.95	-0.0630
70.9	1.86	-0.0646

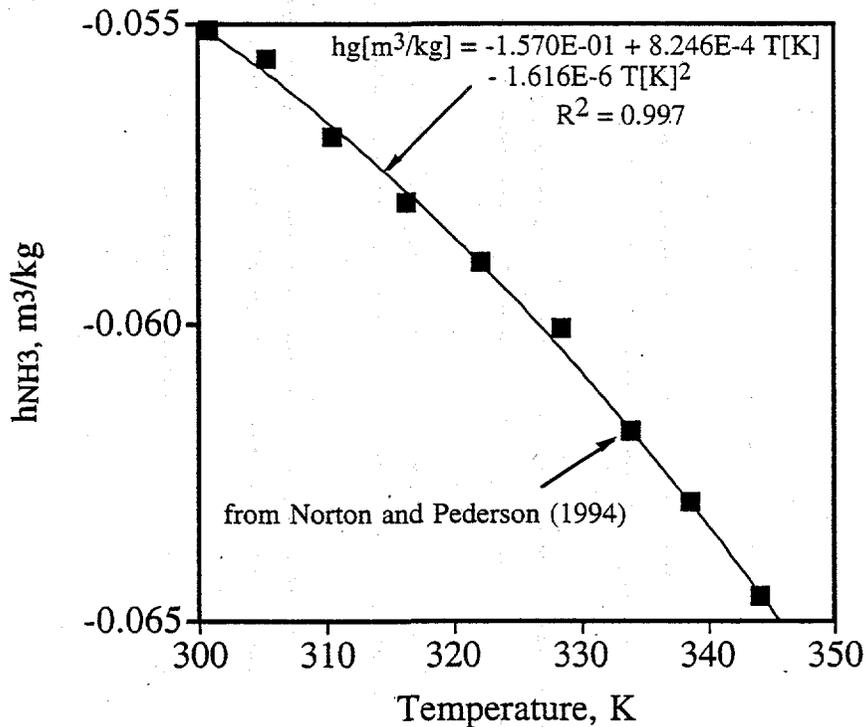


Figure 4.2. Schumpe Model Gas Interaction Parameters for Simulant SY1-SIM-93B Consistent with Ammonia Solubility Data of Norton and Pederson (1994)

Table 4.7. Henry's Law Constants for the Mother Liquor of Tank 241-SY-101 Calculated Using the Schumpe Model with Modified Gas Interaction Constants*

Temperature, °C	K _H ** oxygen	K _H nitrogen	K _H hydrogen	K _H methane	K _H nitrous oxide	K _H ammonia
20	1.52E-05	4.79E-06	2.32E-05	6.34E-06	5.83E-04	10.56
25	1.40E-05	4.45E-06	2.25E-05	5.77E-06	5.03E-04	8.61
30	1.29E-05	4.17E-06	2.20E-05	5.31E-06	4.38E-04	6.96
35	1.21E-05	3.94E-06	2.15E-05	4.93E-06	3.85E-04	5.67
40	1.14E-05	3.76E-06	2.12E-05	4.62E-06	3.42E-04	4.66
45	1.08E-05	3.61E-06	2.10E-05	4.37E-06	3.07E-04	3.86
50	1.03E-05	3.48E-06	2.09E-05	4.17E-06	2.78E-04	3.23
55	9.91E-06	3.40E-06	2.09E-05	4.01E-06	2.53E-04	2.72
60	9.57E-06	3.33E-06	2.09E-05	3.88E-06	2.32E-04	2.31

*Calculated using activity coefficients given in Table 4.2.
 **Units of K_H are mole/kg H₂O-atm.

constants for hydrogen, nitrogen, and nitrous oxide are given in Table 4.8, expressed in the original units of atm-liter waste/mole. Henry's Law constants are also given in units consistent with the geochemistry literature, moles/kg water-atm, assuming an average density of 1.46 g/cm³ and a water weight fraction of 0.361 (see Table 4.1). Substantially higher estimates of nitrogen and nitrous oxide solubilities in Hanford Site wastes are obtained when using the Pasamehmetoglu et al. (1994) model with recommended parameters than when using the Schumpe model with either the set of parameters given in Appendix A or those in Table 4.4. The Pasamehmetoglu et al. (1994) model thus is the more conservative of the two approaches.

A conservative estimate of the inventories of gases dissolved in the wastes in Tank 241-SY-101 can be obtained by using Equation (1), the various Henry's Law constants given above, and the partial pressure of each gas. The best estimate of the overall gas composition in Tank 241-SY-101 is: 28.8 mole % hydrogen, 24.5% nitrous oxide, 11.0% ammonia, 32.8 % nitrogen, 0.35% methane, 0.25% carbon monoxide, and 2.4% water (DOE 1994). For the purpose of estimation, it is assumed that the liquid portion of the waste is in equilibrium with the above gas composition at a pressure of 2 atm. It is further conservatively assumed that the wastes are in equilibrium with oxygen from the air. Oxygen has not been detected in gases released from Tank 241-SY-101. Even though oxygen can be produced radiolytically (Meisel et al. 1993), that gas is likely consumed in chemical reactions with organic waste components. The volume of the wastes is taken as 4 million liters at an average density of 1.6 g/cm³, while the water content is taken as 38.0 wt % (Herting et al. 1992a). As an example, the estimated quantity of nitrogen that may be dissolved in the entire Tank 241-SY-101 at 45°C is:

$$\text{Water present in the entire tank} = [4 \times 10^6 \text{ liters waste}] \times [1.6 \text{ kg waste/1 liter waste}] \\ \times [0.38 \text{ kg water/1 kg waste}] = 2.4 \times 10^6 \text{ kg water}$$

Table 4.8. Estimated Henry's Law Constants for Hydrogen, Nitrogen, Nitrous Oxide, and Ammonia in Hanford Site Waste Mixtures (calculated from Pasamehmetoglu et al. 1994)

Temperature [°C]	K _H [atm-liter/mole] hydrogen	K _H * [mole/kg water-atm] hydrogen	K _H [atm-liter/mole] nitrogen	K _H * [mole/kg water-atm] nitrogen	K _H [atm-liter/mole] nitrous oxide	K _H * [mole/kg water-atm] nitrous oxide	K _H [atm-liter/mole] ammonia	K _H [mole/kg water-atm] ammonia
30	6360	2.98E-04	7880	2.41E-04	219	8.66E-03	0.071	26.7
40	11300	1.68E-04	14800	1.28E-04	450	4.22E-03	0.160	11.8
50	19400	9.78E-05	26800	7.08E-05	877	2.16E-03	0.350	5.4
60	32600	5.82E-05	46400	4.09E-05	1630	1.16E-03	0.740	2.6

*Assumes a liquid density of 1.46 g/cm³ and a water fraction of 0.361 (see Table 4.1).

Nitrogen dissolved in the entire tank at 45°C = [3.61 x 10⁻⁶ moles/kg water-atm (from Table 4.7)]
 x [2.4 x 10⁶ kg water] x [32.8 % nitrogen]
 x [2 atm nitrogen/100% nitrogen]
 ≈ 5.7 moles nitrogen dissolved/tank
 ≈ 128 liters or 4.5 cubic feet.

The estimated quantity of each of the five gases that could be dissolved in the entire waste tank using the Henry's Law constants of Table 4.7 are given in Table 4.9. From Table 4.9, predicted total quantities of methane, oxygen, hydrogen, and nitrogen are quite small. Even their instantaneous release from the wastes would be of no consequence. Of the gases oxygen, nitrogen, nitrous oxide, hydrogen, and methane, nitrous oxide is by far the most soluble. All of the dissolved nitrous oxide released instantaneously would account for only about 10% of a typical Gas Release Event (GRE), however (10,000 cubic feet release x 24.5% nitrous oxide ≈ 2,500 cubic feet of nitrous oxide released versus ≈ 260 cubic feet of nitrous oxide dissolved in the entire tank at 50°C). Of course, it is improbable that all dissolved gases in a large waste tank could be instantaneously released. Further, the entire tank is unlikely to remain in equilibrium with gas bubbles present in the lower, non-convecting layer. In the upper, convecting layer, dissolved gas concentrations should be considerably lower.

For ammonia, the situation is quite different than for the other five gases considered in this study. If it is assumed that the entire waste tank is in equilibrium with gas bubbles containing 11.0% ammonia (DOE 1994) at a total pressure of 2 atm, sufficient ammonia would be present to yield millions of cubic feet of ammonia gas (see Table 4.10). Alternatively, an ammonia concentration in Tank 241-SY-101 wastes of 1 wt% would correspond to 3.0 million cubic feet of ammonia gas that could be produced (4 million liters of waste x 1600 grams of waste per liter x 1 wt% ammonia x 17 grams ammonia per mole ammonia x 0.79 SCF ammonia per mole ammonia = 3.0 million SCF). While the quantity of ammonia expected to be present in the wastes is certainly high, there is no credible mechanism by which even a substantial portion of this ammonia can be converted from the dissolved to the gaseous state and then released from the tank. The ammonia inventory in Tank 241-SY-101 and in other Hanford wastes is worthy of consideration, however, in the development of waste treatment scenarios.

Table 4.9. Estimated Quantity of Gas Dissolved in Entire Tank 241-SY-101 Wastes Assuming All of the Wastes are in Equilibrium with Trapped Gases or With Air, Calculated Using Schumpe Model*

Temperature, °C	Oxygen [SCF]	Nitrogen [SCF]	Hydrogen [SCF]	Methane [SCF]	Nitrous oxide [SCF]	Ammonia [SCF]
20	6.1	6.0	25.3	0.084	541	4.40E+06
25	5.6	5.5	24.6	0.077	467	3.59E+06
30	5.1	5.2	24.0	0.071	407	2.90E+06
35	4.8	4.9	23.5	0.066	357	2.36E+06
40	4.5	4.7	23.2	0.061	317	1.94E+06
45	4.3	4.5	22.9	0.058	285	1.60E+06
50	4.1	4.3	22.8	0.055	258	1.35E+06
55	4.0	4.2	22.8	0.053	235	1.13E+06
60	3.8	4.1	22.8	0.052	215	0.96E+06

*Henry's Law constants taken from Table 4.8.

When the larger Henry's Law constants of Table 4.8 are used in a similar estimate, given in Table 4.10, the possible consequences of dissolved gases are less easily dismissed. Quantities of nitrogen and hydrogen, though much higher than the estimates given in Table 4.9, still are small compared to a typical GRE. Predicted quantities of dissolved nitrous oxide in the entire waste tank, however, are comparable to the nitrous oxide component of a typical GRE. As before, the entire tank is unlikely to remain at equilibrium with gas bubbles trapped in the lower, non-convecting layer; an instantaneous release of all dissolved gases is considered improbable.

Of the two sets of Henry's Law constants (Tables 4.7 and 4.8), those given in Table 4.8 are in much better agreement with experimental solubilities determined in this study than for the gases nitrogen, hydrogen, and nitrous oxide. Those given in Table 4.7 consistently gave predicted solubilities one or more orders of magnitude higher than was observed in the simulated wastes except for ammonia. The two sets of Henry's Law constants for ammonia, however, are in quite good agreement. Due to the better agreement in the experimental data, the Henry's Law constants given in Table 4.8 are thus judged to be the most reliable.

Table 4.10. Estimated Quantity of Gas Dissolved in Entire Tank 241-SY-101 Wastes Assuming All of the Wastes are in Equilibrium with Trapped Gases, Calculated Using Modified Pitzer Model*

Temperature, °C	Nitrogen [SCF]	Hydrogen [SCF]	Nitrous oxide [SCF]	Ammonia [SCF]
30	300	326	8039	11.1E+06
40	160	184	3918	4.92E+06
50	88	107	2005	2.25E+06
60	51.0	63.6	1077	1.08E+06
*Henry's Law constants taken from Table 4.8, from Pasamehmetoglu et al. (1994).				

5.0 Summary and Conclusions

The solubilities of the gases oxygen, nitrogen, hydrogen, methane, and nitrous oxide were measured at several temperatures in the simulated waste composition SY1-SIM-93B. Ammonia solubilities in this simulant were reported previously (Norton and Pederson 1994). The simulant SY1-SIM-93B contains the major components of Tank 241-SY-101: sodium hydroxide, sodium nitrite, sodium nitrate, sodium aluminate, and sodium carbonate. This simulant is a homogeneous solution, the choice of which eliminates complications associated with a changing electrolyte concentration as a function of temperature that would be encountered when using a slurry simulant. Dissolution is one of the means by which gases may be retained in Hanford Site wastes. While models are available to estimate gas solubilities in electrolyte solutions, few data are in existence that pertain to highly concentrated, multicomponent electrolytes such as those stored in Hanford Site waste tanks.

Laboratory equipment was designed and constructed to allow the volume of gases dissolved to be measured directly, without the reliance of calculation of uptake volumes based on pressure/volume relationships. The laboratory apparatus was capable of measuring gas uptake volumes of a few tenths of a mL, essential for work with concentrated brines where solubilities are much reduced when compared to pure water. A two-chambered sample vessel was an essential feature of the solubility apparatus, which avoided artifacts associated with the local condensation and re-equilibration of water vapor. Most of the apparatus was submerged in a well-stirred water bath to maintain thermal equilibrium within $\approx 0.1^\circ\text{C}$.

Experimentally determined gas solubilities were compared with literature models, wherever possible. Models considered were the Pitzer ion interaction model (Pitzer 1987; 1990), a modified Pitzer model (Pasamehmetoglu et al. 1994), and the Schumpe model (Schumpe 1993; Hermann, Dewes, and Schumpe 1995). Each of these models utilize specific interaction parameters that are derived from experimental data, usually for solutions containing one electrolyte. All are a refinement of the well-known Sechenov Equation. With the exception of Pitzer model parameters for oxygen, no information on the temperature dependence of ion interaction parameters was available.

Experimentally determined oxygen solubilities in SY1-SIM-93B were in relatively good agreement with the Pitzer model and with the Schumpe model. Solubilities in the simulant mixture were lowered by approximately a factor of ten relative to solubilities in pure water. Clegg and Brimblecombe (1990) have given detailed Pitzer ion interaction parameters for oxygen, including a first-order temperature dependence of the interaction terms; this gave the best fit to present data. The Schumpe model agreed very well with the Pitzer model (used with ion interaction parameters from Clegg and Brimblecombe (1990) at low temperatures, but tended to slightly underestimate oxygen solubilities at higher temperatures.

Experimental hydrogen solubilities were reasonably well described by the Schumpe model, but were considerably smaller than predictions of the modified Pitzer model (Pasamehmetoglu et al. 1994). Hydrogen solubilities were lowered in the simulant by approximately a factor of 5 to 7. No detailed Pitzer ion interaction parameters, including a temperature dependence, were available for hydrogen in multicomponent electrolyte solutions.

Experimentally determined nitrogen solubilities also were well described by the Schumpe model, and were lowered by approximately a factor of 10 when compared to pure water. As was the case for hydrogen, the modified Pitzer model led to an overestimate of the expected solubility by approximately a factor of three. Detailed Pitzer ion interaction parameters, including a temperature dependence, were not available for nitrogen dissolved in concentrated, multicomponent electrolyte solutions.

Methane solubilities were also lowered in the simulated waste mixture by approximately a factor of 10 compared to solubilities in pure water. Parameters were available only for the Schumpe model, which provided solubility estimates in reasonably good agreement with experimental results.

Nitrous oxide solubilities were a factor of 5 to 7 times less in the simulated waste mixture than in pure water. Agreement with predictions of the Schumpe model were good. Experimental results were approximately a factor of 3 smaller than predictions of the modified Pitzer model (Pasamehmetoglu et al. 1994). Nitrous oxide is the most soluble of the five gases included in this study, by 1 to 2 orders of magnitude.

Ammonia solubilities showed the smallest "salting-out" effect of all the gases considered in this study. In the simulant SY1-SIM-93B, the ammonia solubility was diminished only by a factor of 2 compared to pure water. At 25°C, the Pitzer interaction model (Clegg and Brimblecombe 1989), the Schumpe model (Hermann, Dewes, and Schumpe 1995), and a modified Pitzer model (Pasamehmetoglu et al. 1994) all predicted ammonia solubilities that agreed well with experimental data. All three models underestimate ammonia solubilities at higher temperatures, however.

Inventories of gases (oxygen, hydrogen, nitrogen, methane, nitrous oxide, and ammonia) that could be dissolved in the wastes contained in Tank 241-SY-101 were estimated, based on experimentally determined solubilities from this study in combination with the Schumpe model and the modified Pitzer model. It was assumed in these calculations that the entire waste was in equilibrium with gas bubbles trapped in the lower, non-convecting layer, certainly a conservative assumption. For oxygen, it was assumed that the waste tank was fully equilibrated with air, also a very conservative assumption. For all but nitrous oxide and ammonia, the total estimated inventory of dissolved gases was very small, less than 100 SCF for the entire tank, based on the Schumpe model and gas-specific interaction parameters modified to be consistent with present solubility data. The total quantity of nitrous oxide that could be dissolved in the entire waste tank accounted for approximately 10% of that released in a typical GRE. Ammonia quantities corresponding to more than a million SCF are calculated to be present following the same approach. While very large, there is no credible scenario by which ammonia could be instantaneously released. Excluding ammonia where good agreement was obtained, dissolved gas inventories estimated using the modified Pitzer model (Pasamehmetoglu et al. 1994) were approximately a factor of 10 higher than those obtained using the Schumpe model. Because of the better agreement of present experimental results with the Schumpe model, that model and its associated interaction parameters are considered to be more reliable.

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Appendix A

**Ion-Specific Parameters h_i and Gas-Specific Parameters h_g
Used to Estimate Gas Solubilities in Simulated Waste Mixtures**

Appendix A

Ion-Specific Parameters h_i and Gas-Specific Parameters h_g Used to Estimate Gas Solubilities in Simulated Waste Mixtures*

Ion	h_i [m ³ /kmole]	Gas	h_g [m ³ /kmole]
Na ⁺	0.1079	N ₂ O	-0.0100
OH ⁻	0.0918	O ₂	0.0000
CO ₃ ²⁻	0.1558	H ₂	-0.0176
NO ₂ ⁻	0.0726	CH ₄	0.0028
NO ₃ ⁻	0.0136	N ₂	0.0002
AlO ₂ ⁻	(0.1)**	NH ₃	-0.0506
Fe ²⁺	0.1694		
Cr ³⁺	0.0578		
Ca ²⁺	0.1543		

*From Hermann, Dewes, and Schumpe (1995), valid at 298.2 K.
**No information was available for AlO₂⁻; the indicated value is an estimate.

Appendix B

Pitzer Ion-Interaction Parameters for Oxygen Solubility in Electrolyte Solutions

Appendix B

Pitzer Ion-Interaction Parameters for Oxygen Solubility in Electrolyte Solutions

Table B.1. Parameter $\lambda_{O_2,i}$
 $\lambda_{O_2,i} = a + b/T + c/T^2 + dT^2$

Ion	a*	b	c	d	²⁹⁸ $\lambda_{O_2,i}$
Na ⁺	-0.39548	141.307	--	9.19882E-7	0.1602
OH ⁻	0.99318	-430.552	49860.8	--	0.0500
NO ₃ ⁻	-0.0377	--	--	--	-0.0377
NO ₂ ⁻	(-0.0377)	--	--	--	(-0.0377)
AlO ₂ ⁻	(0.99318)	(-430.552)	(49860.8)	--	(0.0500)
CO ₃ ²⁻	1.0258	-277.074	--	--	0.0964

*Parameters in parentheses are estimates.

Table B.2. Parameter $\zeta_{O_2,ca}$
 $\zeta_{O_2,ca} = a + b/T + c/T^2$

Salt	a*	b	c	²⁹⁸ $\zeta_{O_2,ca}$
NaOH	-0.0125	--	--	-0.0125
NaNO ₃	-0.0120	--	--	-0.0120
NaNO ₂	(-0.0120)	--	--	(-0.0120)
NaAlO ₂	(-0.0125)	--	--	(-0.0125)
Na ₂ CO ₃	-0.0181	--	--	(-0.0181)

*Parameters in parentheses are estimates.

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