

Optimizing Sour Qualification Testing – Verification of H₂S Solubility from H₂S/N₂ Gas Mixtures up to 20,000 psig at 70 °F

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Traditionally, the H₂S partial pressure (P_{H_2S}) of the gas phase has been used as the primary sour severity metric for material qualification and selection under ANSI/NACE MR0175/ISO 15156 guidelines. While the P_{H_2S} is appropriate for characterizing low total pressure systems, the strict, or ideal, Henry's Law approach leads to over estimation of the dissolved H₂S concentration (C_{H_2S}) for high-pressure, high-temperature (HPHT) wells by up to ~20 times at 70 °F. Alternatively, the Ensemble Henry's Law equation corrects for the non-ideal phase behavior of H₂S at HPHT conditions and avoids over-estimation of C_{H_2S} . Given the industry's reliance on using thermodynamic models to evaluate sour HPHT systems, an investigation was initiated to determine the accuracy these model calculations.

An empirical program was undertaken to verify C_{H_2S} predictions for the H₂S-N₂-H₂O system. Multiple 2.7-L C-276 lined autoclaves were charged with a fixed inventory of H₂S in N₂ at multiple total pressure steps, with increasing N₂ pressure, between 30 and 20,000 psig at 70 ± 5 °F. Per total pressure step, H₂S levels in both the liquid and gas phases were measured using common H₂S sampling techniques (H₂S-specific colorimetric tubes and iodometric titration, respectively), following ANSI/NACE TM0177-2016 guidelines. The results were used to calculate total pressure corrected (apparent) H₂S solubility coefficients ($^A k_{H_2S}$). Very good agreement was observed between empirically and computationally derived $^A k_{H_2S}$ values.

Key words: ANSI/NACE TM0177-2016, ANSI/NACE TM0284-2016, Sour testing, Ensemble Henry's Law, Ionic-equation of state (EOS) frameworks, H₂S solubility, Iodometric titration.

INTRODUCTION

A major challenge facing users when designing mildly sour high-pressure, high temperature (HPHT) wells is selecting materials that have both the required mechanical strength and resistance to potential environmentally assisted cracking (EAC) threats, particularly sulfide stress cracking (SSC). Key to optimizing material selection for sour service conditions is to accurately characterize the environmental severity of HPHT wellbores based the compositional analyses of the brine and hydrocarbon gas streams.

During the 1950s and 1960s, initial investigation of carbon and low alloy steels exposed to H_2S revealed that susceptibility to SSC was influenced by the dissolved H_2S concentration in the aqueous phase (C_{H_2S}) for certain steels hardened to > 22 HRC at atmospheric pressure.^{1, 2} However, the ability to measure and/or predict C_{H_2S} at full wellbore pressure was in its infancy in 1975. Therefore, an alternative sour severity metric to C_{H_2S} was sought. Both low-pressure SSC test results¹⁻⁵ and field observations⁶⁻⁸ revealed an apparent trend of increasing SSC susceptibility with increasing H_2S partial pressure (P_{H_2S}). This motivated the architects of the original NACE MR-01-75⁹ standard in 1975 to define environmental severity based on P_{H_2S} , which can be easily assessed from limited environmental field data.

While P_{H_2S} is appropriate surrogate for C_{H_2S} for low total pressure systems, recently P_{H_2S} has been demonstrated to over predict the corresponding C_{H_2S} by at least an order of magnitude at 10,000 psia and 70 °F.^{10, 11} Despite its many shortcomings, P_{H_2S} remains the primary sour severity metric in ANSI/NACE MR0175/ISO 15156-2015¹² (herein, referred to as the Standard¹²). However, recognizing the complications with using P_{H_2S} , the recent publication of ISO 15156-2:2015/Cir.1:2017 now permits users the option to define sour severity by alternative metrics: fugacity (f_{H_2S}),¹³⁻¹⁵ activity (a_{H_2S}),¹⁶ and concentration (C_{H_2S}).^{11, 17-19} These modern sour severity metrics may expand the application ranges of commercial materials in sour systems while maintaining reasonable, but not excessive, margins of safety.

Unlike P_{H_2S} , however, the modern sour severity metrics are usually calculated from advanced thermodynamic models, formally referred to as ionic-equation of state (EOS) frameworks. These frameworks are often semi-empirical in nature and are calibrated against experimentally derived thermochemical databases.²⁰⁻²² While sour ionic-EOS frameworks are gaining acceptance,^{11, 14, 15, 23} there are two potential concerns: Firstly, there are only a handful experimental H_2S solubility databases available, with the majority of measurements made at total pressures $< 5,000$ psi (< 345 bar) and at $P_{H_2S} >> 10$ psia.^{21, 24-31} Therefore, using these databases to predict mildly sour phase behavior at 10,000 to 20,000 psig requires extrapolation by several orders of magnitude. Secondly, there are few empirical studies independently verifying the accuracy of sour predictions at total pressures $> 5,000$ psig.^{10, 21, 27}

In an attempt to evaluate the reliability of ionic-EOS frameworks for predicting sour severity of high-pressure systems, this paper discusses an empirical approach to quantify the relationship between C_{H_2S} and P_{H_2S} with total pressure. For this project, the authors evaluated the H_2S - H_2O - N_2 “laboratory” system (a common surrogate of the typical H_2S - H_2O - CH_4 “oilfield” system) from 30 to 20,000 psig at 70 ± 5 °F. A 2.7-L C-276 lined autoclave rated for sour service up to 20,000 psig, with a fixed charge of H_2S , was then pressurized with nitrogen at incremental total pressure steps from 30 psig to 20,000 psig. Multiple determinations of the gas and liquid phase H_2S concentrations were made at each total pressure step using techniques optimized by the authors. The measured C_{H_2S}/P_{H_2S} set per total pressure step were then used to calculate a total-pressure corrected solubility coefficient ($^A k_{H_2S}$), an empirically derived parameter that could be used to benchmark ionic-EOS frameworks.

As far as the authors are aware, this paper is the first publication of H_2S solubility data up to 20,000 psig (1,380 bar $\equiv$ 138 MPa). In addition to verification of ionic-EOS frameworks for sour systems, this paper also demonstrates the precision and accuracy of the H_2S sampling and analysis techniques adopted from the ANSI/NACE TM0177-2016³² and ANSI/NACE TM0284-2016³³ standards for this project.

Review of the Historical and Modern Sour Severity Metrics

The architects of the original NACE MR-01-75 standard,⁹ first adopted in 1976, recognized that SSC was the result of the combination of: 1) A susceptible metallurgy; 2) The applied stress (tensile load); and 3) The C_{H_2S} in an acidic aqueous solution.^{1, 8, 34, 35} In 1975, both the complex thermodynamic models required to calculate C_{H_2S} under actual high-pressure wellbore conditions and personal computers powerful enough to run the complex mathematical algorithms were decades into the future. Therefore, the architects simplified the dissolved H_2S problem by assuming that ideal gas law behavior applied. It was further assumed that C_{H_2S} was linearly proportional to the P_{H_2S} with total pressure (see Figure 1a).^{9, 36} In addition, H_2S solubility ($'k_{H_2S}$, the ratio of C_{H_2S}/P_{H_2S}) was assumed to be independent of both the total pressure (see Figure 1b) and of interactions with other molecules in the gas phase. Collectively, these concepts formalized the " P_{H_2S} Paradigm," a term coined by the authors.

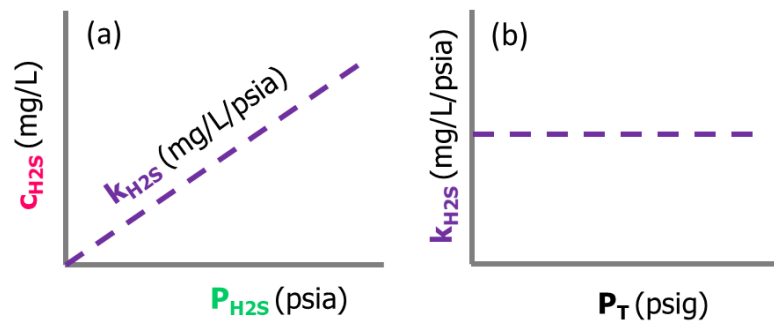


Figure 1. Historical H_2S solubility assumptions based on the P_{H_2S} Paradigm.

Historical P_{H_2S} Paradigm—Strict Henry's Law Approach

The P_{H_2S} is defined as the mole fraction of H_2S in the gas phase (y_{H_2S}) multiplied by the total pressure (P_T):

$$P_{H_2S} = y_{H_2S} P_T \quad (3)$$

The use of P_{H_2S} as the sour severity metric assumes that P_{H_2S} is proportional to C_{H_2S} via the Strict (Ideal) Henry's Law constant ($'k_{H_2S}$):

$$C_{H_2S} = 'k_{H_2S} P_{H_2S} = 'k_{H_2S} y_{H_2S} P_T \quad (4)$$

where $'k_{H_2S} = 230 \text{ mg/L/psia}$ (0.1 mol/L/atm) for freshwater at 75°F and 14.7 psia .^{11, 37-40} Assuming that ideal gas behavior governs over the entire total pressure range for oil and gas systems, the C_{H_2S} - P_{H_2S} relationship increases linearly with increasing P_{H_2S} with a constant slope of $'k_{H_2S}$ (Figure 1a). Thus, $'k_{H_2S}$ is independent of increasing P_T (Figure 1b). These assumptions were considered reasonable in 1975, because P_{H_2S} is a relatively accurate approximation for C_{H_2S} at room temperature and low total pressures for dilute solutions.

The primary objective of researchers in the 1950s to 1970s was not to replicate the actual wellbore sour phase behavior during sour qualification tests,⁴¹ but rather to select relatively severe laboratory environments for evaluating metallurgical factors.^{34, 35, 42, 43} In addition, the operating pressures of the original SSC well failures were $< 5,000 \text{ psig}$ ⁸ and the vast majority of in-service failures were associated with wells producing $> 3.5 \text{ mol\%}$ ($> 35,000 \text{ mol ppm}$) H_2S .⁴⁴ Without going into detail, compensating for the effect of total pressure on H_2S solubility for systems clearly identified as sour would have only had a marginal benefit in terms of optimizing material selection, at the time.

Forty-five years later, however, the increased reliance on high-strength materials, which typically have an enhanced sensitivity to H₂S compared to their lower yield strength analogs, and increased accessibility of commercial ionic-EOS frameworks have facilitated a paradigm shift from defining sour severity on the basis of P_{H2S} to that of either f_{H2S} ,¹³⁻¹⁵ a_{H2S} ,¹⁶ and/or C_{H2S} ^{11, 17-19} metrics that better reflect actual sour severity of HPHT systems.

Modern Sour Severity Metrics—Ensemble Henry's Law Approach

Regardless of the preferred sour severity metric, core to all the modern metrics is the “Ensemble Henry's Law equation”.⁴⁵ The Ensemble Henry's Law is an extension of the Strict Henry's Law (Equation 4), and incorporates three important thermodynamic correction factors to account for the change in H₂S solubility with total pressure.^{38, 46} To emphasize the aqueous (left-hand-side of equation) and hydrocarbon (right-hand-side of equation) based thermodynamic parameters, the equation may be written as:

$$C_{H2S} \gamma_{H2S} = I_{H2S} \phi_{H2S} \exp[\xi] P_{H2S} \quad (5)$$

where γ_{H2S} is the activity coefficient (ionic strength correction), ϕ_{H2S} represents the fugacity coefficient (gas phase correction), and $\exp[\xi]$ refers to the Poynting (total pressure correction) factor on gas solubility in the aqueous phase.^{14, 15, 23} (A “Glossary of Thermodynamic Parameters” is included at the end of this paper.)

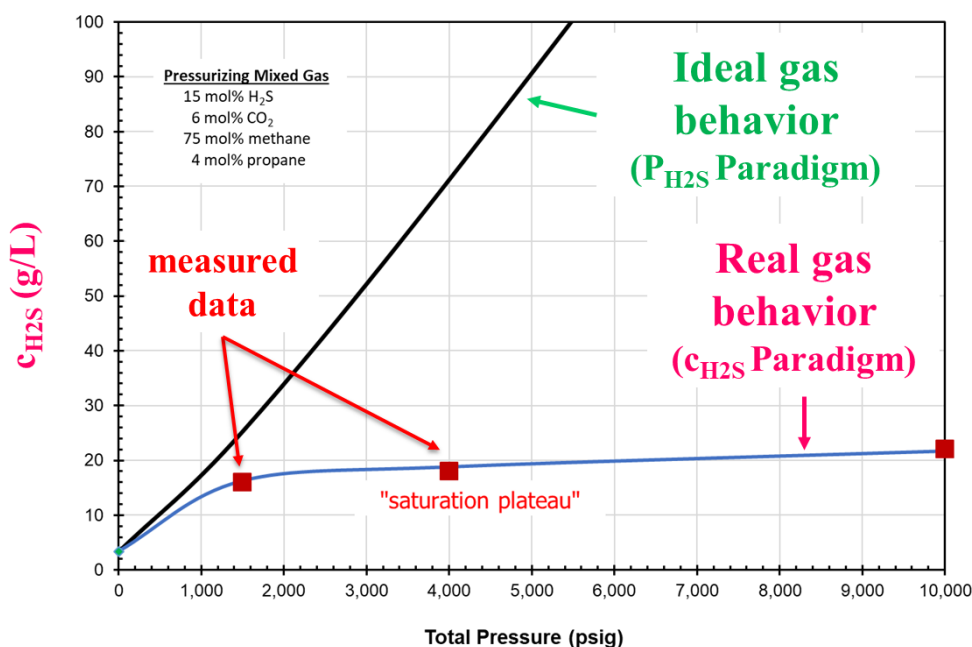


Figure 2. Goodness-of-fit comparison of the P_{H2S} and C_{H2S} paradigms to experimental data.¹⁰

Figure 2 compares the predicted values for C_{H2S} obtained using the Ensemble Henry's Law Equation (solid blue curve) and the ideal gas law predictions of the P_{H2S} Paradigm (black line) with experimental data (red squares) up to 10,000 psia. The following observations can be made:

- The agreement between the experimental data and C_{H2S} predicted by the Ensemble Henry's Law Equation are excellent,
- Whereas, the experimental value of C_{H2S} at P_T=10,000 psig was ~10% of the value predicted by the ideal gas law.

- These observations were later confirmed by Kumar *et al.* in 2013²⁷ at C_{H_2S} values relevant for mildly sour wells.

Figure 2 also exhibits a flatline or “saturation plateau” in the C_{H_2S} , between 1,800 and 10,000 psia for the methane-rich system, which has been observed by others.^{20, 23, 25, 26, 47} This “saturation plateau” occurs due to the limited solubility of H_2S in the aqueous phase, eventually reaching saturation. Within this “saturation plateau” region, the C_{H_2S} is nearly independent of P_T ,¹⁴ strongly suggesting that C_{H_2S} is a stable parameter that could be used as a reliable, scalable sour severity metric from atmospheric pressure to at least 10,000 psia.¹⁰

The Ensemble Henry’s Law is often coded into ionic-EOS frameworks, which are usually validated against published H_2S solubility data. Unlike the CO_2 - H_2O -salt system,²² there are only a handful of reliable H_2S - H_2O -salt databases available,^{21, 24-31} and the majority of the public datasets contain experimental data only up to 5,000 psig.²⁰ (Excluding this paper, at the time of publication, the authors are not aware of any published experimental solubility H_2S - N_2 - H_2O -salt data performed above 10,000 psia.)⁽¹⁾

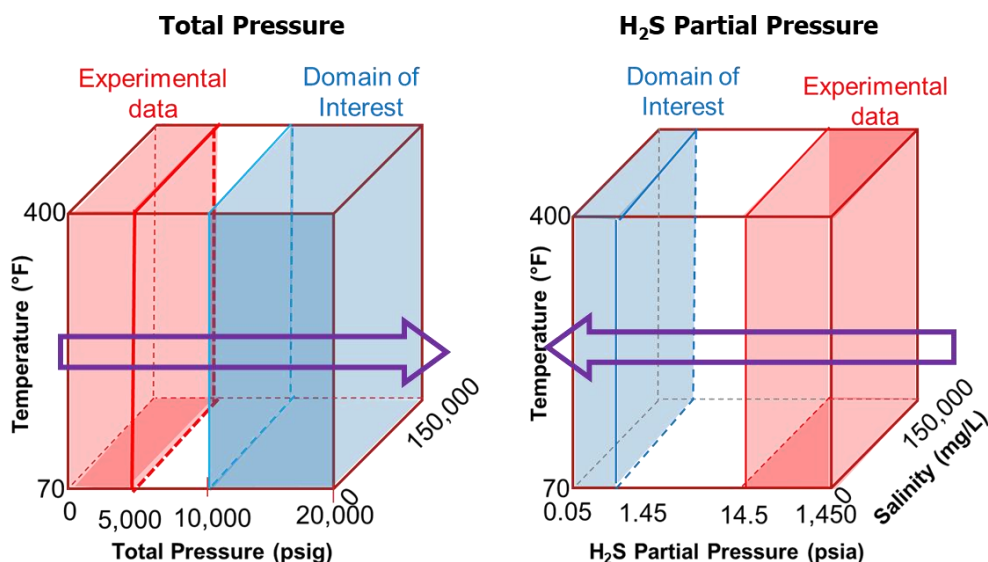


Figure 3. Schematic comparison between the available H_2S - H_2O -Salt public database domain versus the HPHT sour service domain of interest.¹¹ Arrows indicate the direction and magnitude of extrapolation.

Consequently, the reference H_2S data were obtained at much higher P_{H_2S} and much lower P_T than the HPHT domain of interest,^{17-19, 23, 4} as shown in Figure 3. As a result, there are significant extrapolations from current reference data when modeling mildly sour HPHT conditions, potentially resulting in calculation errors. Independent validation of calculated H_2S solubility data under mildly sour conditions to 20,000 psig is therefore needed to extend confidence in the predictions of the current ionic-EOS frameworks to the HPHT domain.

⁽¹⁾ In the articles cited, optical spectroscopy using small, high-pressure cells with optical windows was the classic technique used to measure H_2S solubility.²⁹ Alternative analytical methods used to quantify H_2S solubility include calorimetry^{25, 26} and iodometric titration.⁴⁸ Regardless of analytical technique, the objective of the cited H_2S solubility studies were to quantify the change in H_2S solubility with temperature. (While important, the effect of temperature on H_2S solubility is beyond the scope of this article.) The effect of total pressure on H_2S solubility, while recognized by researchers,^{25, 26} was of secondary importance.

An effective method to evaluate the accuracy of sour predictions involves comparing the computationally and empirically derived H₂S solubility coefficients (k_{H_2S}). Empirically, H₂S solubility can be derived by grouping the thermodynamic parameters together from Equation (5) into Equation (6):

$$C_{H_2S} = \phi_{H_2S} \gamma_{H_2S}^{-1} \exp[\xi] {}^A k_{H_2S} P_{H_2S} \quad (6)$$

This is simplified to Equation (7):

$$C_{H_2S} = {}^A k_{H_2S} \cdot P_{H_2S} \quad (7)$$

where ${}^A k_{H_2S}$ represents the Real (apparent) H₂S Henry's Law Coefficient. ${}^A k_{H_2S}$ has the units of mg/L/psia⁽²⁾, when P_{H_2S} is in psia, and C_{H_2S} has the dimension of mg/L.^{38, 46, 49} The ${}^A k_{H_2S}$ is temperature, total pressure, and salinity dependent due to non-ideal solubility effects.⁵⁰ At normal pressure and temperature (NPT), ${}^A k_{H_2S}$ equals ${}^I k_{H_2S}$. As temperature and/or total pressure increase, ${}^A k_{H_2S}$ decreases.

The following sections of this article describe an internal study to experimentally benchmark calculated ${}^A k_{H_2S}$ values in 10,000 mg/L Cl⁻ from 30 psig to 20,000 psig at 70 ± 5 °F.

Empirical H₂S-N₂-H₂O Solubility Study at 70 ± 5 °F

The objectives of this empirical H₂S solubility study were:

- 1) To investigate the effect of total pressure on H₂S solubility in the H₂S-H₂O-N₂ system at total pressures between 30 and 20,000 psig at 70 ± 5 °F.
- 2) To verify the analytical reproducibility when measuring the concentration of H₂S of both the liquid (C_{H_2S}) and headspace gas (y_{H_2S}) phases by iodometric titration and H₂S-specific colorimetric tubes, respectively, in accordance ANSI/NACE TM0177-2016 procedures³² modified to positively exclude air, thus preventing loss of H₂S.
- 3) To empirically derive ${}^A k_{H_2S}$ (i.e., the ratio of measured C_{H_2S} / ($y_{H_2S} \times P_T$) values) between 30 to 20,000 psig at 70 ± 5 °F.
- 4) Compare the experimental results to the predictions of a commercial sour ionic-EOS framework.

Table 1. H₂S-N₂-H₂O system investigated.

Aqueous Phase	Gas Phase	Temperature	Total pressure	No. of individual total pressure steps
10,000 mg/L Cl ⁻ + 445 mg/L acetic acid and <i>in situ</i> pH of 3.4	0.02 mol H ₂ S was sourced from 10 mol% H ₂ S in N ₂	70 ± 5 °F (20 ± 3 °C)	30 to 20,000 psig (2 to 1,380 barg)	13

Table 1 shows the environmental test parameters evaluated during this project. Since the purpose of this project was focused on quantifying ${}^A k_{H_2S}$ up to 20,000 psig, and not evaluating a material's susceptibility to a specific sour environment, typical ANSI/NACE[†] TM0177-2016³² test specimens were not included in the test design. For this study, ultrahigh purity (UHP) N₂ was used as a surrogate for methane to boost

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⁽²⁾ Following the United States customary (USC) units convention.