

ACID BASE CHEMISTRY IMPLICATIONS FOR ALKANOLAMINE GAS TREATING

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Steven Fulk, PhD.
Trimeric Corporation
PO Box 826
Buda, Texas USA 78610
+1 512-557-5338
steven.fulk@trimeric.com

Kevin Fisher, P.E.
Trimeric Corporation
PO Box 826
Buda, Texas USA 78610
+1 512-431-6323
kevin.fisher@trimeric.com

Clay Jones, P.E.
Trimeric Corporation
PO Box 826
Buda, Texas USA 78610
+1 737-704-6246
clay.jones@trimeric.com

ABSTRACT

Acid-base reaction chemistry is the principal phenomenon behind the successful application of aqueous alkanolamine solutions in gas treating. Common gas contaminants H₂S and CO₂ are acidic when dissolved in water. These contaminants are commonly called “acid gases.” Acid gases can be effectively removed from gas streams by reaction with the alkanolamine in the aqueous solution. Since the reaction is between a weak acid and a weak base, it is readily reversed in a regenerator column.

This paper will discuss the fundamentals of acid-base reactions, including a review of pH, pK_a, pK_b, and the common ion effect. The primary chemistry of acid gases with aqueous alkanolamine solvents will be discussed followed by the effects of additional strong acids (Heat Stable Salts and Stripping Promoters). The acid gases H₂S and CO₂ have different acidic strength, and we will briefly discuss how their different acidity - along with the different time scales of their reaction kinetics - influences selective treating processes.

Having discussed the influence of strong acids on amine systems, we conclude with a discussion of how strong bases can be used as stripping promoters for weak, volatile bases such as NH₃.

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Steven Fulk, PhD., Trimeric Corporation, Buda, TX
Kevin Fisher, P.E., Trimeric Corporation, Buda, TX
Clay Jones, P.E., Trimeric Corporation, Buda, TX

Introduction

This paper is a “back to basics” discussion of acid-base reactions and the important role they play in gas treating. We begin with a general discussion of chemistry and provide definitions for common terms such as pK_a , pK_b , and pH. The paper concludes with high-level, but practical, discussions of common industrial situations where chemistry controls the behavior of the process.

Gas Treating Overview

The term *gas treating* refers to, among other things, the removal of H_2S and CO_2 from industrial gas streams. The two contaminants H_2S and CO_2 are commonly referred to as *acid gases* because when they dissolve in water, they acidify the solution. In practice, there are other acid gases that can be important, e.g., SO_2 and NO_2 , but for the purposes of this paper the term “acid gases” refers exclusively to H_2S and CO_2 .

Gas treating by counter-current contact with a solution of alkanolamine and water exploits the acidity of the acid gases. Mixtures of alkanolamine and water are commonly referred to simply as *amine*. Amine solvent provides a weakly basic – or alkaline – liquid which chemically reacts with, and loosely holds, the acid gases when the gas and liquid come in contact in the contactor column. The weakness of the reaction allows it to be readily reversed to strip out the acid gases in the regenerator column.

Without the chemical reaction, amines can hold very little acid gas. Therefore, it is important that the amine solution retains its alkalinity to preserve its ability to remove acid gas. In real operating units, strong acid contaminants or chemical additives neutralize the alkalinity of the amine. Unlike weak acid gases, the reaction of strong acids with amines is not readily reversible in the regenerator. However, the net impact of losing some alkalinity is not always bad; when the fundamentals of the chemistry are understood, the addition of a strong acid can lead to better system performance through enhanced/promoted stripping performance.

Acid Base Reactions

This paper will focus on eight components, each of which participate in ionic reactions as listed in Table 1.

Table 1 - Ionic Reactions. All values from [1] except MDEA which is from [2].

Component	Ionic Reactions	Equilibrium Parameter at 77°F
Water	$H_2O \xrightleftharpoons{K_w} H^+ + OH^-$	$pK_w = 14.00$
H ₂ S	$H_2S \xrightleftharpoons{K_{a1}} H^+ + HS^-$ $HS^- \xrightleftharpoons{K_{a2}} H^+ + S^{2-}$	$pK_{a1} = 7.00$ $pK_{a2} = 12.92$
CO ₂	$CO_2 + H_2O \xrightleftharpoons{K_{a1}} H^+ + HCO_3^-$ $HCO_3^- \xrightleftharpoons{K_{a2}} H^+ + CO_3^{2-}$	$pK_{a1} = 6.35$ $pK_{a2} = 10.25$
Formic Acid	$HCOOH \xrightleftharpoons{K_a} H^+ + HCOO^-$	$pK_a = 3.75$
Phosphoric Acid	$H_3PO_4 \xrightleftharpoons{K_{a1}} H^+ + H_2PO_4^-$ $H_2PO_4^- \xrightleftharpoons{K_{a2}} H^+ + HPO_4^{2-}$ $HPO_4^{2-} \xrightleftharpoons{K_{a3}} H^+ + PO_4^{3-}$	$pK_{a1} = 2.23$ $pK_{a2} = 7.21$ $pK_{a3} = 12.32$
MDEA	$MDEA + H_2O \xrightleftharpoons{K_b} MDEAH^+ + OH^-$ $MDEA + H^+ \xrightleftharpoons{K_{b'}} MDEAH^+$	$pK_b = 5.5$ $pK_{b'} = -8.5$
Ammonia	$NH_3 + H_2O \xrightleftharpoons{K_b} NH_4^+ + OH^-$ $NH_3 + H^+ \xrightleftharpoons{K_{b'}} NH_4^+$	$pK_b = 4.75$ $pK_{b'} = -9.25$
Caustic	$NaOH \rightarrow Na^+ + OH^-$	N/A

Note that all these reactions (save one) are *reversible* as indicated by the double-headed arrows. If a reaction is reversible then there will be some amount of both products and reactants in the liquid. Caustic is the lone exception because whenever caustic is added to water, it immediately and completely dissociates into ions – the molecule NaOH can exist as a solid, but not as a dissolved molecule in water.

How far a reversible reaction proceeds to the right of a reaction equation is described by an equilibrium parameter, usually found in literature as a reaction K. Notice however that the acids (H₂S, CO₂, formic acid, and phosphoric acid) have a K_a parameter and produce an H⁺ ion as a reaction product whereas the bases (MDEA and Ammonia) have a K_b parameter and consume an H⁺ ion as a reactant. Water is a unique case: its reaction is written to look like an acid since the H⁺ ion is a reaction product, but its equilibrium parameter is called K_w due to the special importance of water in aqueous chemistry.

An aqueous solution that has compounds that undergo reversible reactions will contain some amount of each ionic species listed in all of the reactions for that compound. The distribution of ions in a solution is called the solution's speciation. Details of speciation calculations are beyond the scope of this paper.

Equilibrium K Parameter

The meaning of the K parameter is a numerical ratio of product concentrations divided by reactant concentrations. Equation 1 shows the reaction of formic acid as an example. Larger values of K indicate that a reaction proceeds further to the right; smaller values mean that a reaction does not proceed as far.

The bracketed terms in Equation 1 represent the concentration of each species measured in units of molarity (moles of species per liter of solution). For rigorous calculations on typical industrial solutions with significant total ionic concentration, the *activity* of the species should be used instead of molarity to account for non-idealities in real electrolyte solutions.

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

Equation 1 – Equilibrium K parameter for formic acid

Numerical values for K_a and K_b are usually very far from 1, so as a matter of convenience they are expressed as pK_a and pK_b as defined in Equation 2 and Equation 3 to make the numerical values easier to manage. For example, at 77°F the value of K_a for formic acid is 1.77×10^{-4} whereas the pK_a value is 3.75.

$$pK_a = -\log_{10}(K_a)$$

Equation 2 - Definition of pK_a

$$pK_b = -\log_{10}(K_b)$$

Equation 3 - Definition of pK_b

A common, and usually easy to measure, parameter that provides significant information about aqueous solutions is the pH, which is related to the concentration of H^+ ions by Equation 4. Concentration of H^+ is measured in units of molarity. Again, when non-idealities are significant, the activity of the H^+ ion more accurately represents the solution.

$$pH = -\log_{10}([H^+])$$

Equation 4 - Definition of pH

The relationship of pK_a to pH gives insight into speciation of an acid in solution. Comparing Equation 2 and Equation 4, we see that pK_a is the same as pH any time the value of $[H^+]$ is the same as the value of K_a . Using formic acid as an example (Equation 1), we see that any time $[HCOO^-]$ and $[HCOOH]$ have the same value, then the values of $[H^+]$ and K_a will be the same as well. The conclusion we draw from this comparison is: the pK_a value of an acid tells us what pH makes the acid 50% dissociated. At room temperature, the pK_a of H_2S is 7.0, therefore if H_2S is in a solution with $pH > 7.0$ then it will mostly be dissociated. Conversely if H_2S is dissolved in a solution with $pH < 7.0$ then the H_2S will mostly exist as molecular H_2S . A stronger acid like formic acid has a pK_a of 3.8, meaning that the solution must be more acidic for molecular formic acid to be present in significant amounts. Note that this relationship is approximate, not

precise, but it is a useful rule of thumb. The rigorous form of this relationship accounts for non-idealities.

$$K_a = \frac{[H^+][\cancel{HCOO^-}]}{[\cancel{HCOOH}]} = [H^+]$$

Equation 5 - Relationship between pK_a and pH. The values of pK_a and pH are the same when $[HCOO^-]$ and $[HCOOH]$ are equal, meaning the acid is 50% dissociated. Therefore, pK_a tells us the pH value where the acid is 50% dissociated. As a rule of thumb: When $pH > pK_a$, the acid is mostly dissociated into charged ions. When $pH < pK_a$, the acid is mostly in its uncharged state.

Common Ion Effect

The reason that pH, or H^+ concentration, is such a meaningful value is that the H^+ ion appears in almost every reaction listed in Table 1. Knowing the pH of a solution tells you something about all of those reactions.

Figure 1 shows an overview of how ionic chemistry affects the solubility of H_2S through the common ion effect. Beginning at the left hand of the figure, we see that H_2S is in phase equilibrium between the vapor and liquid phases. Uncharged H_2S molecules in the vapor and liquid phases come to equilibrium according to Henry's Law. This is referred to as H_2S 's *physical solubility*.

Once in the liquid phase, a portion of the H_2S will dissociate into HS^- and H^+ ions. All H_2S molecules that transform into a charged HS^- ion are *chemically bound* in the liquid phase as long as they're in the charged state. Henry's Law applies only to H_2S , not HS^- or S^{2-} . The amount of H_2S that dissolves into the liquid when this mechanism is accounted for called H_2S 's *chemical solubility*. Since H_2S is a weak acid, its chemical solubility in water is only around twice as high as its physical solubility – meaning that only about half of the H_2S molecules transform into charged ions in neutral water.

The chemical solubility of H_2S can be greatly enhanced by adding a base such as MDEA to the solution. As shown in Figure 1, MDEA is a base which can hold H^+ ions generated from dissolved H_2S . Once an H^+ ion is attached to MDEA, it cannot rejoin with HS^- to reconstruct the volatile, uncharged H_2S molecule. In the presence of MDEA, an H_2S molecule that enters the liquid phase and dissociates into HS^- is likely to be trapped in the liquid phase. In lean amine streams, this effect can increase the chemical solubility of H_2S to become hundreds or thousands of times greater than its physical solubility alone. In rich amine streams where the total H_2S concentration is higher, the chemical solubility effect is smaller but can still be 5 to 10 times greater than physical solubility.

This mechanism of reactions interacting with each other is referred to as the *common ion effect*. The acidic reaction of H_2S produces H^+ ions, and the basic reaction of MDEA consumes those H^+ ions. When both of H_2S and MDEA are in solution together, these reactions will proceed to a much greater extent because of the common ion effect. **The net impact of having a base in solution is to increase the solubility of H_2S .**

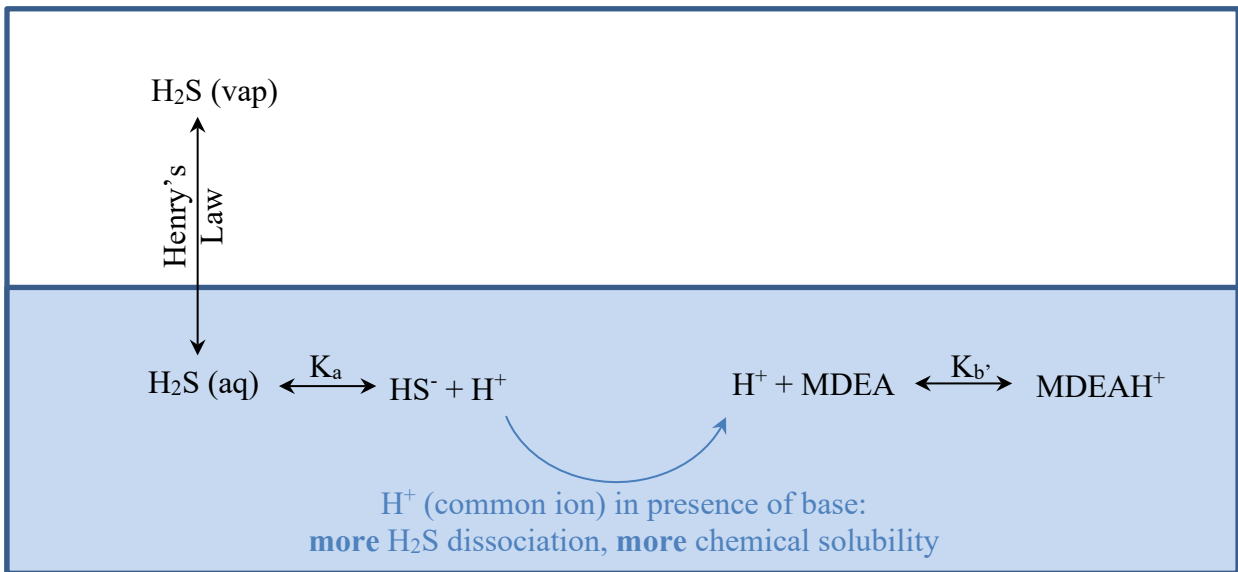


Figure 1 - H₂S solubility and the common ion effect

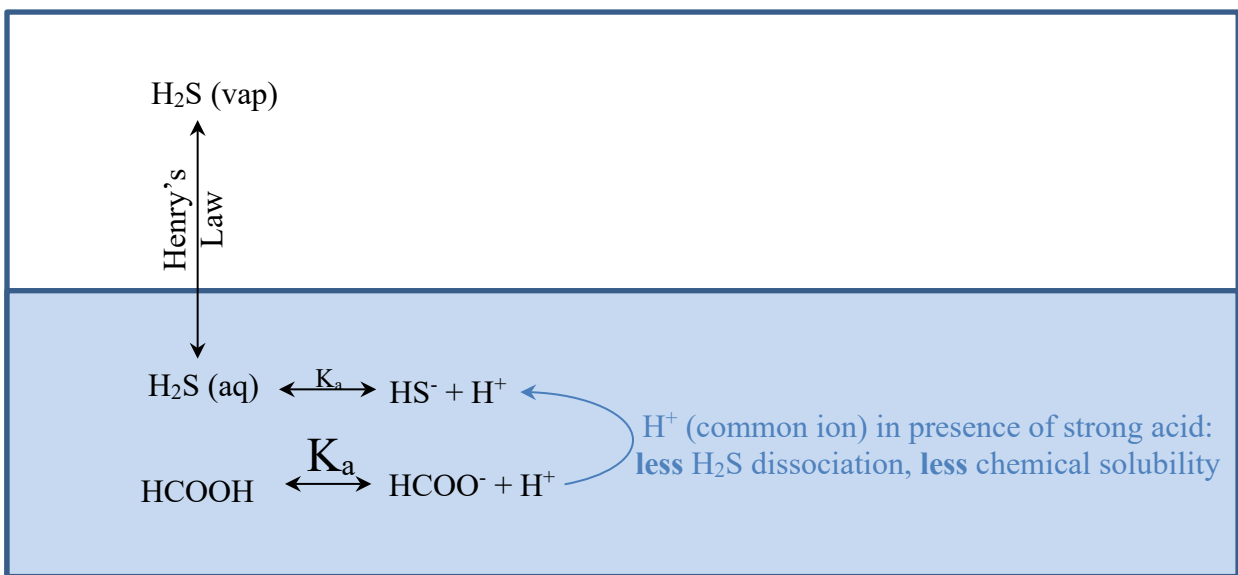


Figure 2 – H₂S and HSS, common ion effect

Figure 2 shows the impact of the common ion impact on H₂S solubility in the presence of a stronger acid. In this example, H₂S is in solution with formic acid (HCOOH). Both H₂S and formic acid have similar ionic reactions, where the acid molecule dissociates into a negatively charged ion and an H⁺ ion. The difference is that formic acid is a much stronger acid than H₂S, as indicated visually by the small K_a for H₂S and large K_a for formic acid shown in the figure. Formic acid's large K_a means that it will produce an abundance of H⁺ ions, and these excess H⁺ ions will find any available HS⁻ ions and join with them to create uncharged H₂S molecules. **The net effect of having a strong acid in solution is to decrease the solubility of H₂S.**

These two influences of the common ion effect are key to understanding the chemistry of gas treating. When trying to capture acid gases in an aqueous solution, the solubility will be *increased* by the presence of bases which *increase* the amount of ionic dissociation of the acid gases. Conversely, the solubility will be *decreased* by the presence of stronger acids that *decrease* the amount of ionic dissociation. Stated another way, any time an acid gas is highly dissociated, its chemical solubility will be much greater than its physical solubility, and when there is not much ionic dissociation then its chemical and physical solubilities will be nearly the same.

Heat Stable Salts

Acid gases form *heat regenerable* salts when they react with amines, but stronger acids form salts that are not heat regenerable. These salts are commonly referred to as Heat Stable Salts (HSSs). These strong acids can't be stripped out in the regenerator column, which is why they're commonly referred to as "heat stable". These contaminants tend to accumulate in the amine over time because they are non-volatile. HSSs must be dealt with in the liquid phase using reclaiming, ion exchange, or other methods.

In Figure 2, we established that stronger acids reduce the chemical solubility of acid gases and therefore make acid gases less soluble in amines. However, the impact of stronger acids on the treating in an industrial amine unit is not as straight forward. HSS are truly a double-edged sword. Higher HSS concentrations hurt in the absorber column where we're trying to absorb acid gases, but they help in the regenerator column where we're trying to desorb acid gases. Conversely, lower HSS concentrations (e.g., from reclaiming) help pick up more acid gas in the absorber column but make it harder to strip acid gas in the regenerator column.

Figure 3 is the first of several graphs showing how the common ion effect influences H₂S in solution. The data for all such figures in this paper were generated using Aspen Plus V11 using the electrolyte NRTL-RK model with default interactions. The simulations describe the behavior of acids dissolved in 45 wt% MDEA at 77°F and 1 atm. The y-axis of these charts shows the solubility boost from chemical reaction (chemical solubility) relative to simple physical solubility of H₂S.

Figure 3 shows how different concentrations of a common strong acid HSS (formate) affect dissolved H₂S. For all three formate concentrations studied (0, 5,000, and 15,000 ppmw), the presence of formate suppresses the dissociation of H₂S which reduces its chemical solubility. We see that the magnitude of this effect is very different at different levels of H₂S loading. At low H₂S loadings below 0.001 – 0.0001 mol/mol, the presence of formate reduces chemical solubility by a factor of more than 10x. At higher H₂S loadings above 0.5 mol/mol, the increase is much less pronounced at just 1.1x.

The conclusion is that **HSS always make acid gases less soluble in amine, but the effect is much more severe at lower acid gas loadings.**

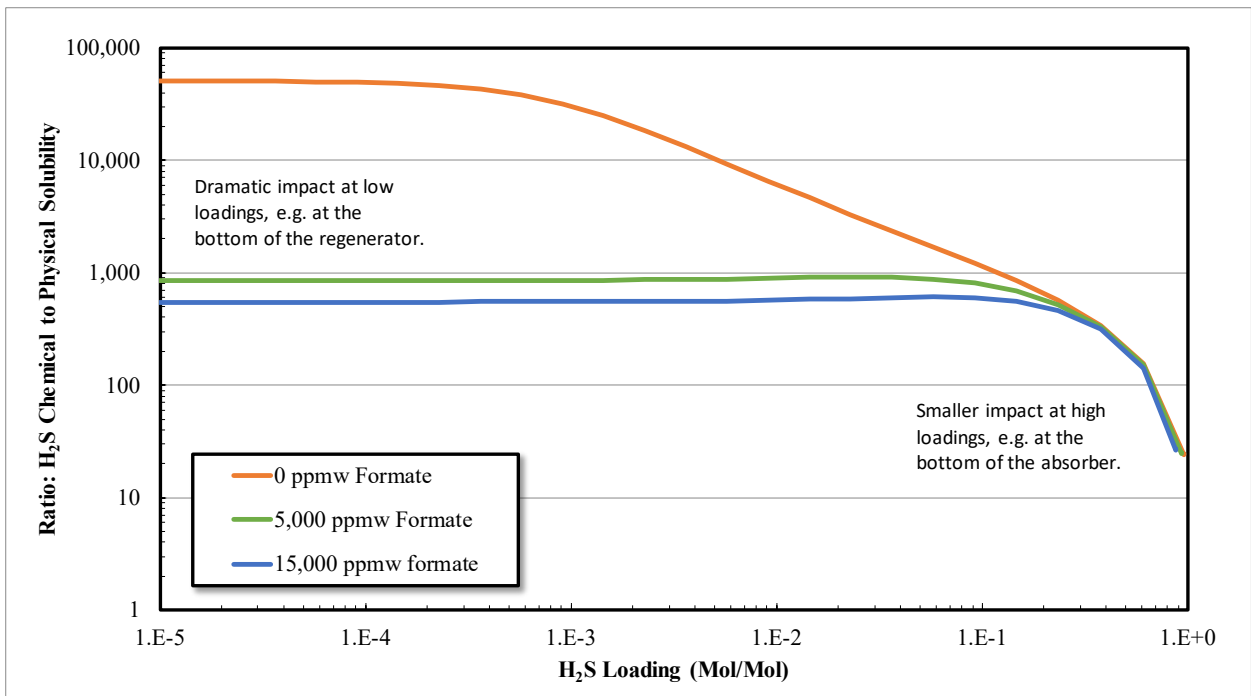


Figure 3 - Effect of HSS (Formate) on H₂S Solubility in Amine

While HSS are strong acids that accumulate naturally in a circulating amine, stripping promoters are strong acids *intentionally added* because of their ability to help the regenerator strip almost all of the acid gas and achieve very low lean loadings.

Figure 4 shows the effect that a common stripping promoter (phosphate) has on dissolved H₂S. Comparing Figure 3 with Figure 4, we find that HSS and stripping promoters have the same kind of impact on H₂S: They greatly reduce H₂S solubility at low loadings and reduce it to smaller extent at high loadings.

Stripping promoters can be a useful additive for amine systems when the treating performance is governed by lean loading, i.e., when the amine absorber is in a lean-end pinch condition. The gas leaving an absorber that is lean end pinched is at equilibrium with the lean solvent. Treating cannot be improved by increasing the solvent rate. Lean-end pinch is a common situation in sulfur plant TGU's where H₂S partial pressure is low, and both lean and rich amine loadings are relatively low too. In such systems, the benefit of lower lean loadings greatly outweighs the negative impact of lower capacity at high loadings.

A key conclusion of this paper is that **both HSS and stripping promoters have the same impact on acid gas solubility.**

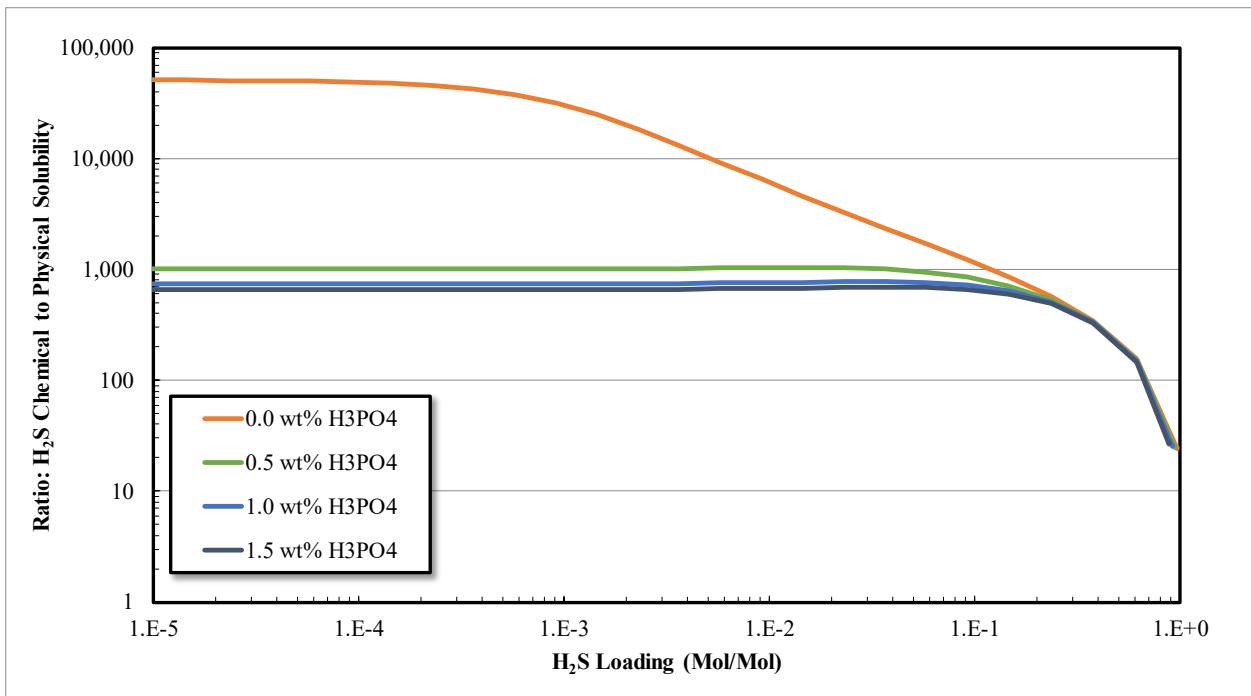


Figure 4 - Effect of Stripping Promoter (Phosphate) on H₂S Solubility in Amine

Selective Treating

In the previous sections, the impact of strong acids on chemical solubility of H₂S was discussed. Stronger acids suppress acidic dissociation of H₂S through the common ion effect. Both HSSs and stripping promoters are strong acids and therefore they effect chemical solubility by the same mechanism. Any acid that is a stronger acid than H₂S would have the same effect. In fact, CO₂, which is also a stronger acid than H₂S, shows the same effect on chemical solubility as the other stronger acids we've studied. However, Figure 5 shows that it takes higher concentrations of CO₂ to generate the same effects because CO₂ is a weaker acid than formate or phosphate.

This interaction between H₂S and CO₂ in amines is important to selective treating applications, where the objective is to absorb as much H₂S as possible and as little CO₂ as possible. As Figure 5 shows, each incremental amount of CO₂ that absorbs in the amine reduces the overall solubility of H₂S. Selective treaters leverage another dimension of chemical reactions: reaction rates. Since CO₂ reaction rates are slower than H₂S, the enhancement of chemical solubility is slower for CO₂ than H₂S. Selective absorbers are sometimes designed with short contact time; a well-designed short absorption bed provides enough trays or packing to pick up the maximum amount of H₂S, but no more beyond that. If too much contact time is provided, CO₂ will eventually make it into the liquid phase and speciate which reduces the solubility of H₂S by the common ion effect.

A counter-intuitive consequence of this relationship is that amine leaving an absorber can contain more than the equilibrium amount of H₂S, i.e., > 100% of equilibrium H₂S loading. Were the amine solvent allowed to come to equilibrium with the sour gas, the additional CO₂ pickup will actually push some of the dissolved H₂S back out of solution through the common

ion effect. **It is possible for a real rich amine stream to contain more H₂S than the equilibrium stream could hold.**

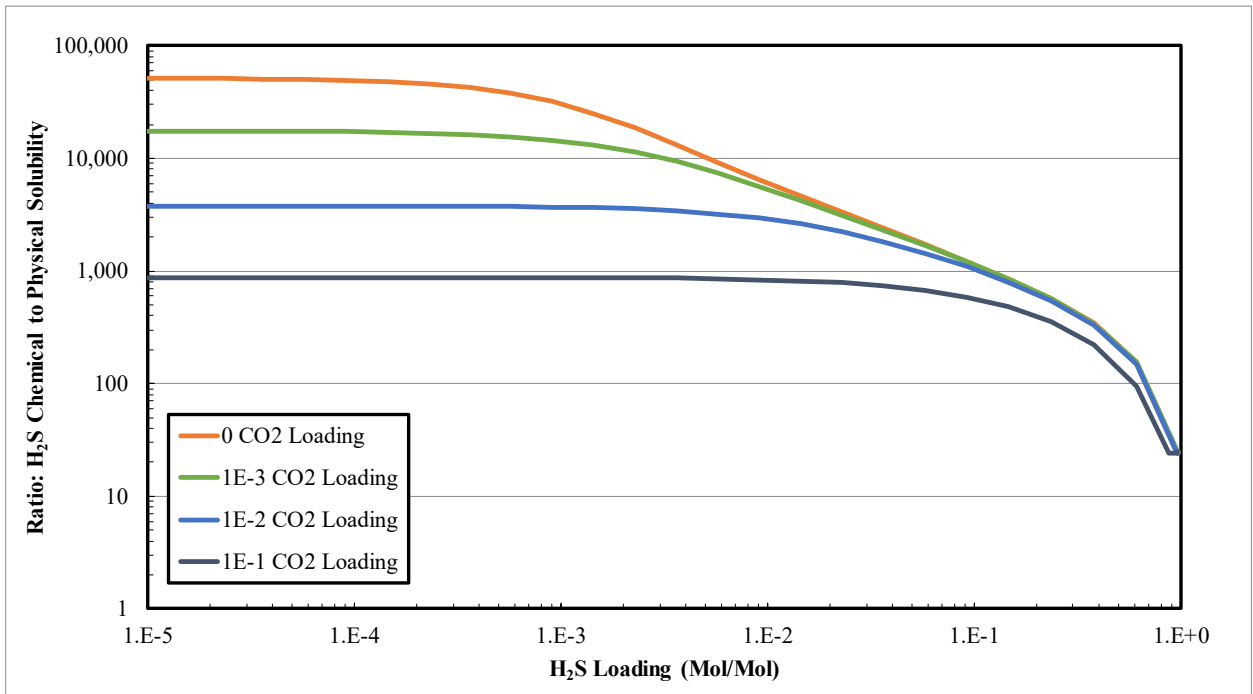


Figure 5 - Effect of CO₂ on H₂S Solubility in Amine

Time Scales

Gas treating is a dynamic process, involving mass transfer, phase change, and chemical reaction – each of these steps proceeds at its own rate. Many factors influence those rates, but the rates can be quite different for each acid gas. These rates have serious practical implications including sizing of equipment, limits on how much removal can be achieved for a particular gas, and the amount of removal of gases relative to each other (removal selectivity).

It is helpful to consider the timescales over which phenomena occur to gain some insights into why some gases can be absorbed faster or to a greater extent than others. Figure 6 illustrates how wide the range of timescales can be for the different physical and chemical phenomena that influence gas treating processes. Since gas treating involves both mass transfer and chemical reaction, the overall rate will be limited by whichever step is slowest.

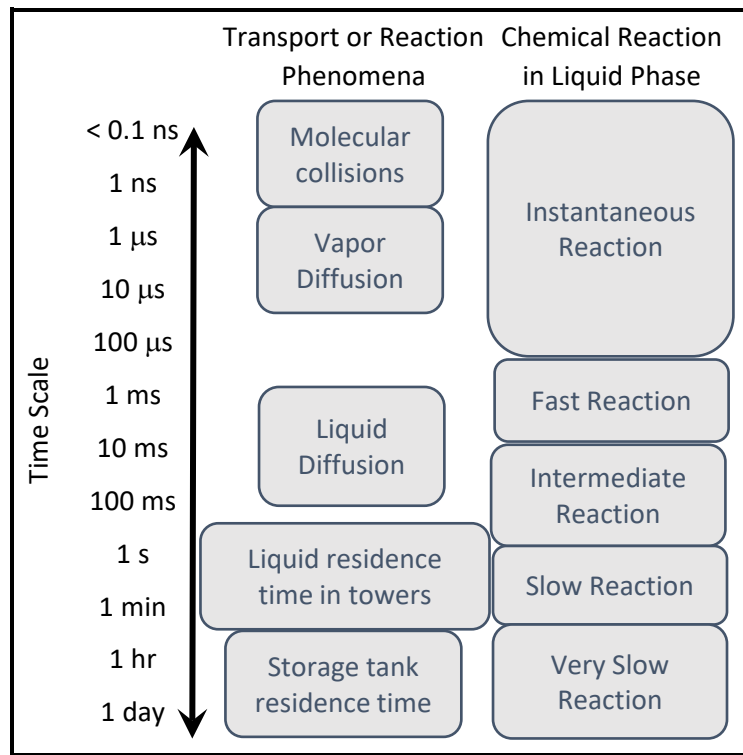
The amount of time between molecular collisions is extremely short, on the order of a tenth of a nanosecond, or roughly 1 ten-billionth of a second. Any chemical reaction that requires the collision of two or more molecules is generally limited to this timescale and cannot proceed any faster. Fast reactions that take place quicker than about 100 microseconds are generally referred to as being “instantaneous” for the practical purpose of industrial gas absorption processes. In this situation, the gas is consumed in a chemical reaction that takes place at the gas-liquid interface and the absorption rate is controlled by the diffusion of the gas through the gas film to the interface. Further increases or improvements in the liquid mass transfer coefficient, the reaction kinetics, or liquid residence time will have minimal effect on the absorption rate.

Familiar examples of systems that approach this ideal are absorption of H₂S or SO₂ into strong caustic solutions.

For chemical reactions that take place in a relatively narrow range from about 1 ms to about 1/10th of a second, the chemical reaction takes place largely in the thin film of liquid that exists near the gas/liquid interface. For “fast” chemical reactions in this range, most of the absorbed gas is consumed by chemical reaction in this diffusion film. For the slightly slower “intermediate” chemical reactions the reaction takes place both in the diffusion film, and to some extent in the bulk liquid [3]. The absorption of H₂S and CO₂ into alkanolamine solutions is a familiar example where fast/intermediate reactions in the diffusion film greatly influence the gas absorption kinetics.

Slow reactions are generally not as common, but for these reactions most of the reaction takes place in the bulk liquid rather than the diffusion film. In these cases, the liquid residence time on the trays or in the liquid held up in the packing is important. An example of a slow to infinitely slow reaction is the absorption of oxygen in aerobic fermenters. In this system, mass transfer is of less importance and the absorption rate is controlled almost entirely by the rate that oxygen is consumed by the microbes [4].

It is possible to take advantage of these differences in chemical reaction behavior of gases being absorbed to strongly influence the relative rates of absorption between the gases. In the context of gas treating, this is commonly applied to achieve selective absorption of H₂S when CO₂ is also present. **For H₂S, the chemical reactions are always at equilibrium, whereas CO₂ reactions take time to achieve equilibrium. The net result is higher rates of absorption for H₂S compared to CO₂.**

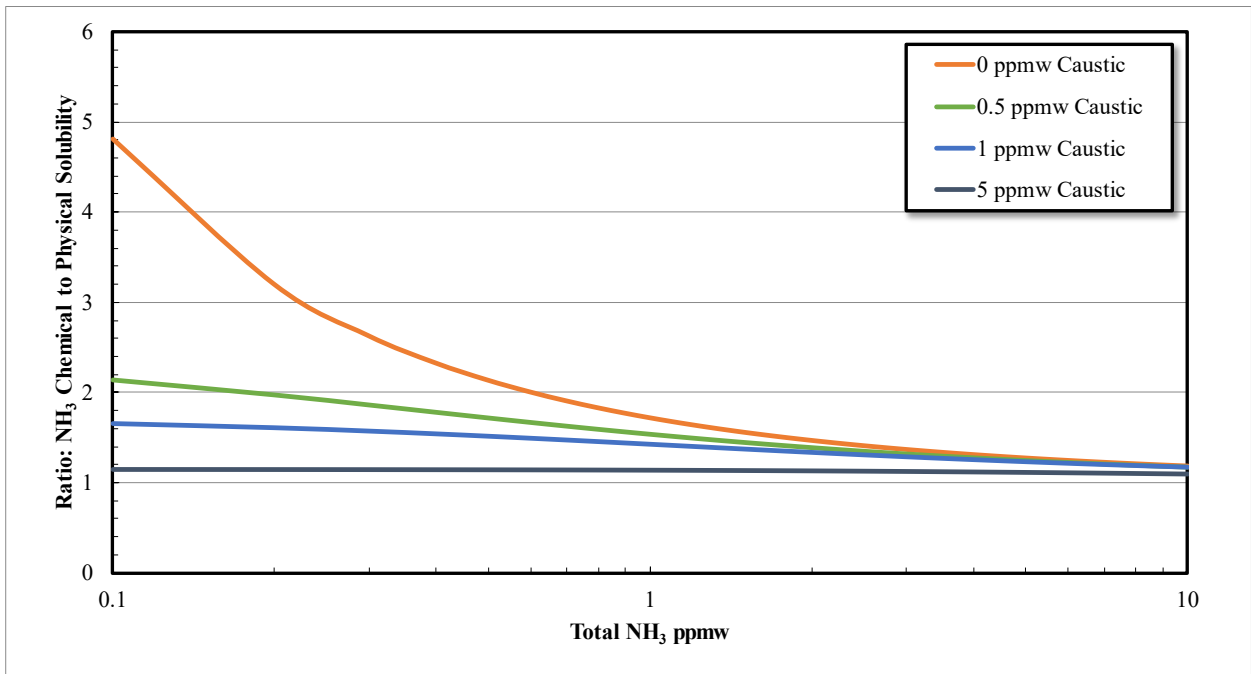


Calculation notes for Figure 6: Diffusion times are based on typical diffusion film thickness (L) of 5 microns, typical liquid diffusion coefficient (D) of 2×10^{-9} m²/sec, and timescale approximately equated to L^2/D , such that $L^2/D = 12.5$ milliseconds. Vapor diffusion coefficients are typically $10^4 - 10^5$ times larger than liquid diffusion coefficients.

Strong Bases

In chemistry, acids and bases are mirror images of each other, so the same behavior can be observed in both classes of chemicals. We previously discussed how the common ion effect strongly influences the absorption of acid gases, but it also strongly affects the absorption of volatile bases. A common example of the common ion effect for bases can be found in Sour Water Strippers (SWSs) where the process objective is to strip dissolved NH₃ out of water.

As shown in Table 1, NH₃ participates in chemical reaction with water. Any NH₃ (ammonia) that gets converted to NH₄⁺ (ammonium) is chemically bound in the liquid and can't be stripped. Just as a strong acid can act as a stripping promoter to help remove acid gases, a strong base can act as a stripping promoter to help remove basic gases. Figure 7 shows how **caustic reduces the solubility of NH₃**.



Conclusion

This paper showed how the fundamentals of acid-base chemistry explain many aspects of practical gas treating.

Heat stable salts and stripping promoters are strong acids which make H₂S less soluble in amine – the lower solubility causes both lower lean loadings and lower rich loadings, but the magnitude of the effect is much more pronounced for lean vs rich amine. For lean-end pinched absorbers, where treating performance is dominated by lean loading, an optimum concentration of these acids will make a big improvement in the stripper which overshadows the small reduction in rich loading (and solvent capacity). In other words, the benefit to the stripper can out-weigh the harm in the absorber.

Since CO₂ is a stronger acid than H₂S, it is possible for CO₂ to act as a “stripping promoter” for H₂S – an undesirable outcome for selective treating applications. Because the chemical reactions for H₂S is faster than for CO₂, it is possible to make design choices (e.g., short contact time) which allow for H₂S absorption to proceed nearly to completion without absorbing very much CO₂.

Finally, we showed that the common ion effect works for both acids and bases. Caustic can act as a stripping promoter to reduce the solubility of NH₃ in a Sour Water Stripper.

Understanding the underlying chemistry puts all of these disparate phenomena into a single consistent framework and shows that they’re all different examples of the same thing: acid-base chemistry and the common ion effect.

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