Applications and Benefits to the Gas Processing Industry of the GPA Research Program

L.G. Lynddon, V.N. Hernandez-Valencia, M.W. Hlavinka and J.A. Bullin,
Bryan Research & Engineering, Inc.,
Bryan,Texas

ABSTRACT

Over the years, the Gas Processors Association (GPA) has appropriated funding toward research that has served the Gas Processing Industry in many ways. Perhaps the most significant manner in which the benefits of this research have been realized is through more accurate measurements of phase equilibria, enthalpy, density, and other physical properties leading to more efficient engineering analysis and design. In particular, the accuracy of process simulators has been dramatically improved since these basic properties are involved in virtually every calculation. This article will review many of the projects undertaken by GPA. The article will provide examples where accurate predictions were not possible for engineering calculations due to lack of data, but today are performed routinely due to data collected under GPA research. Finally, the article will suggest some areas of possible research where current data are limited.

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INTRODUCTION

GPA research projects date back to 1926 with motor fuel volatility research. Much of the early research, prompted by safety concerns, consisted of determination of physical properties and volume correction data. From this collection of data came the publication of the first compilation of equilibrium constants for mixtures of natural gas liquids (NGL), which served to greatly improve the safety of product handling and storage as well as improve efficiency of process design and operations.

In addition to data compilation, GPA research has led to development of product specifications and test methods for natural gas and NGL, including the Reid vapor pressure test, liquefied petroleum gas (LPG) vapor pressure method, and the copper strip corrosion test for LPG. In addition, sampling procedures and analytical methods were developed. Of great importance were the first basic volume correction factors for custody transfer of LPG essential to accurate and equitable custody transfer of natural gas and liquid products. Due to this research, GPA developed standardized calculation procedures for applying physical property data to custody transfer measurements of natural gas and NGL.

Numerous publications based on GPA research are available which are widely used in engineering calculations and designs on a daily basis. Many of the publications, such as the Research Reports, contain data pertaining to phase equilibria for a wide variety of mixtures and conditions including hydrates, enthalpy determinations, and solubility. This information improves the accuracy of engineering design and increases the efficiency of operations for absorption processes, fractionation, cryogenic extraction, and contaminant removal.

In addition to the research reports, the aforementioned measurement, sampling, and analytical method standards

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are published by GP A. These standards are tools used in all facets of gas processing industry operations including compression, transport, storage, custody transfer, heat transfer, etc. The GPSA Engineering Data Book [1] is one of the most commonly used engineering reference books today. Much of the information compiled in the research reports and in other publications has been conveniently incorporated into the Data Book to facilitate engineering calculations. It is considered the "bible" of gas-processing design and operation worldwide [2].

An indirect benefit of GPA research is the funding and training of graduate students in research programs at various universities. After graduation, many of these students have either pursued careers in gas processing or related industries or selected careers in academia where they train undergraduate and graduate students in engineering disciplines. At a minimum, this system has produced engineers that are sensitive to the needs of the gas processing industry.

Accurate data are crucial to accurate engineering calculations. The information contained in research reports is commonly used to modify predictive models to accurately predict phase equilibria and thermodynamic properties for conditions beyond the range of the data. In addition, correlations may be developed which can provide reasonably accurate predictions. The data may be in the form of a chart, as can be found in the GPSA Engineering Data Book, or incorporated in a process simulation program. Table I provides a summary of applications for gas processing and the benefit to the application derived from GPA Research.

Table I
Summary of benefits to the gas processing industry from GPA research

Application	Benefit from GPA Research
Custody Transfer	Standards, tests, and analytical methods that allow safe transport and equitable transactions between buyer and seller
Hydrocarbon Thermodynamics	More efficient liquids recovery process design and operation (eg. high pressure retluxed demethanizer [3], reservoir management. enhanced oil recovery)
Water Removal	Accurate hydrate formation prediction which allows more efficient operation with respect to glycol/methanol circulation or injection rates. Minimization of pollutant emissions by the most economical means.
Acid Gas Removal	More efficient operation with respect to amine type and circulation rate, and ability to design for selective absorption

REVIEW OF GPA RESEARCH PROJECTS

A major portion of GPA's cooperative research has been directed to fundamental thermodynamic properties of hydrocarbon mixtures. Other projects focus on behavior of odorants and contaminants in natural gas, including water and hydrate formation, sour gas components, and treating processes, or solubilities at cryogenic temperatures.

Hydrocarbon Thermodynamics

Research in this area was originally prompted by safety concerns, and more recently by economic concerns. Over half of the 160-plus GP A Research Reports deal with properties and behavior of light hydrocarbons, extremely important to the processing of gas and natural gas liquids. Most of the data contained in the Research Reports consist of phase equilibria and enthalpy determinations for hydrocarbon mixtures or hydrocarbon mixtures containing CO2, H2S or Nitrogen.

Water Removal

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Research in the general area of water removal was prompted by both economic and environmental concerns. This research, including hydrate formation temperatures, is most important since reliable data were not previously available. More than a dozen Research Reports contain hydrate formation data. Of special significance are Research Reports which contain data for hydrate formation in the presence of an inhibitor such as methanol or ethylene glycol (RR-74, RR-87, RR-92, RR-I06, and RR-156). Vapor-liquid and vaporliquid-liquid equilibrium data which help to predict water content of the hydrocarbon as well as the hydrocarbon content of the aqueous phase are also available. More recently, research has been performed on the mutual solubility of methanol or glycols and hydrocarbons. This research was most certainly prompted by recent legislation limiting the amount of aromatic and other contaminants in glycol still vent emissions. The solubility data contained in Research Reports RR-13l (TEG), RR-137 (EG) and RR-149 (EG and Methanol) are invaluable due to lack of other available data on the subject.

Acid Gas Removal

Gas and liquid hydrocarbon sweetening with amines has received considerable interest recently, which has prompted GPA to become more active in amine research, particularly in areas not studied by others. This interest stems from design as well as environmental concerns. The GPA data bank contains solubility of CO2 and H2S in amines and substantial enthalpy of solution data for amines with both CO2 and H2S. Due to the availability of other reliable CO2 and H2S solubility data, GP A research has focused on enthalpy determinations and solubility of organic sulfur contaminants in amines. Some sour water equilibrium data are also available. RR-I04 contains the most complete information on solubility of acid gas in amines and serves to verify data from other sources, while RR-124 deals with DEA at low acid gas loadings. RR-125 contains information on the solubility of acid gas in protonated DEA solutions. The recently released RR-l64 contains data for solubility of organic sulfur compounds (methyl-and ethyl mercaptans and COS) in MDEA and DEA.

IMPROVEMENT OF THE ACCURACY OF ENGINEERING PREDICTIONS

Engineering predictive tools can be divided into three categories: fundamental laws or first principles, structured modeling, and purely empirical correlations. Examples of first principles include ideal gas law, law of gravitation, and the notion of conservation of mass and energy. Predictive parameters for models with first principles can be determined from a purely mathematical basis. No data are required to arrive at the prediction.

Structured modeling includes the equations of state, Virial equations, and transport properties. These models are of a known form and are often modifications of first principles. Data are required to regress the model parameters given the form of the model. For example, observations of vapor-liquid equilibrium can be used to estimate parameters such as critical temperature, critical pressure, and acentric factors. Based on the model selection, it is possible to extrapolate or extend predictions beyond the range of data.

Purely empirical relationships relate one set of observations to other observations. For example, density to temperature. The model form and parameters are based on the "best fit" of a collection of data. These relationships are less extendable than structured models, and the reliability of extrapolated predictions is limited.

The data contained in GP A research reports improve the accuracy of calculations involved in predictions by providing a basis for empirical correlations, and a reference for structured modeling. The Equation of State (EOS) is the most convenient method of calculating thermodynamic properties, and can make predictions outside the range of available data. Since simulators are an important tool in engineering design, the simulator's accuracy is likewise greatly improved by reliable data. In addition to information on pure components, VLE information for mixtures is necessary to develop the mixing rules for accurate predictions by the EOS. The EOS used in a simulator interpolates and extrapolates the data, even with only a few points.

It is common to underestimate the amount of property information required for accurate design of processing equipment. This includes VLE, VLLE, enthalpy, entropy, viscosity, density, thermal conductivity, surface tension, etc. All of these are functions of temperature, pressure, and/or composition. Thus, even with the best of thermodynamic modeling, a considerable amount of experimental data is required for each property. The greater the amount of quality data over temperature, pressure, and composition ranges, the greater the reliability of the predictions.

Hydrocarbon Thermodynamics

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GPA research has improved vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) predictions in a vast number of systems. Consider the following case as an example. For hydrocarbon-water systems containing vapor with a single aqueous liquid phase, the same interaction parameter (kij) may be used to compute water distribution into the vapor phase and hydrocarbon distribution into the liquid phase without introducing noticeable discrepancies between computed and experimental data. On the other hand, VLLE predictions are severely limited when using the same interaction parameter for both phases as illustrated in Figure 1 for the system n-Butane-Methane-Water [4]. The K-values for water (defined as mole fraction water in vapor phase/mole fraction water in hydrocarbon liquid phase) are two orders of magnitude higher than the experimental values. This discrepancy was a limitation for EOS predictions until GP A funded Project 752, which had as one of its objectives to include the interaction of water with hydrocarbons. Upon completion, Research Report 42 [5] clarified the need for including a separate interaction parameter for each phase to handle partial miscibility in water-hydrocarbon systems. For this reason, RR-42 has special importance to the improvement of EOS predictions. The effect of setting different interaction parameters per RR-42 for the interactions for each phase is also shown in Figure 1. Computed K values are very close to the experimental values.

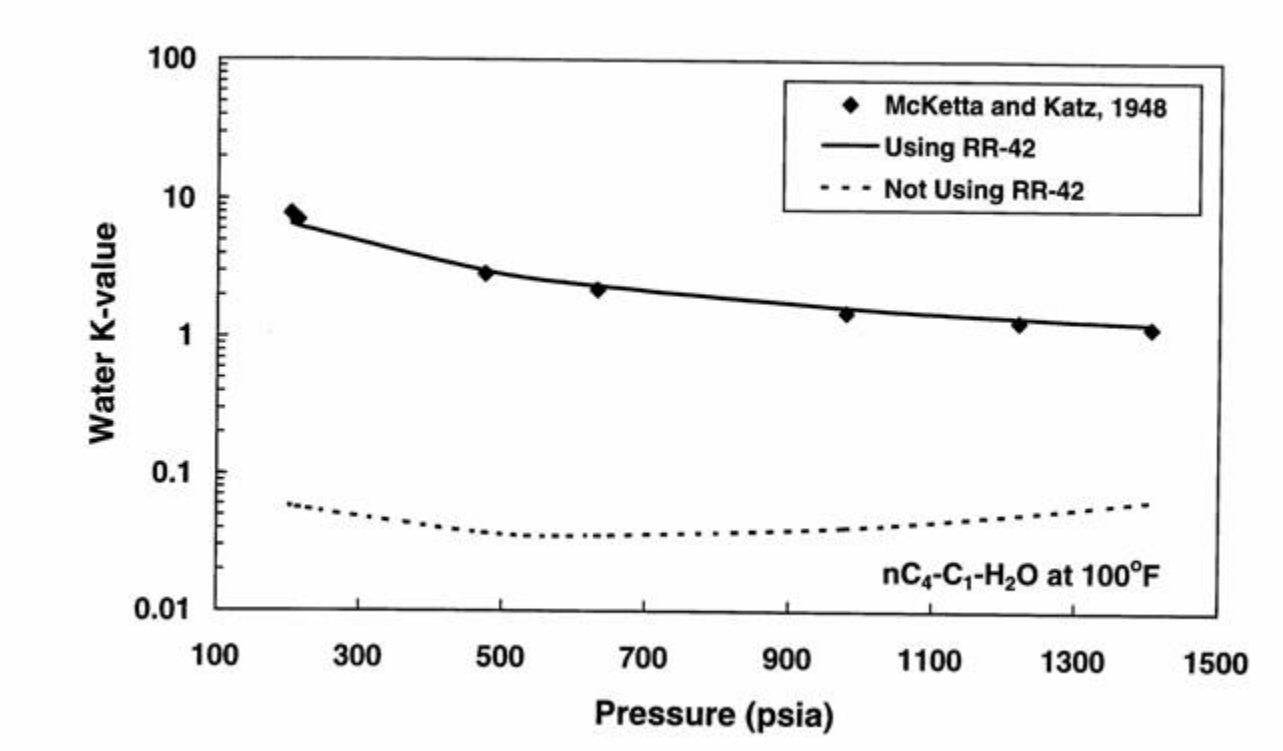

Figure 1. Water K-Value improvement using RR-42

Possibly the most important contribution of fluid property research is that it has allowed the development of new processes and technology [3]. The ambient oil absorption plant for NGL recovery in the 1950' s was replaced by the more efficient refrigerated oil absorption process in the 1970's. Research Reports RR-15, RR-22, RR-25, RR-27, and RR33 contain data which improved low temperature process design. By the 1980' s, the cryogenic expander plant had become the design of choice. These advances are a direct result of low temperature data collected and published by GP A between 1981 and 1987. The series entitled "Liquid-Liquid- Vapor Equilibria in Cryogenic LNG Mixtures" (RR's 49, 60, 67, 79, 91, and 115) contain a wealth of VLE data including systems containing CO_2. CO_2 freezeout in cryogenic processes was a problem due to inaccurate CO_2 solubility data before publication of these and other research reports.

New technology for NGL recovery in the 1970' s included the use of side reboilers on the demethanizer. This improvement resulted in a 30% or greater savings in horsepower as described by Elliot [3]. The designs would not have been possible without data made available through the aforementioned GP A research. This type of design also requires a computer distillation program, so the data were incorporated into process simulators at that time.

More recent technology that has served to increase efficiency even further is the high pressure refluxed demethanizer. A 40% savings in compression can be realized [3]. An added benefit of this process is that it can

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handle high CO_2, which may eliminate the need for CO_2 treating in some cases. The ability to design this type of process was made possible by accurate CO_2 solubility data provided by GPA research.

Water Removal

Supplemental research in the area of water removal was prompted by both environmental and economic concerns. One example of the contribution of GP A research to the improvement of predictions by process simulators is that of BTEX solubility in glycols.

In response to stringent emissions regulations for aromatic compounds benzene, toluene, ethylbenzene, and xylenes, GPA along with API funded research which made possible the accurate prediction of BTEX emissions from glycol still vents. In fact, after incorporating data for BTEX solubility in glycols [6] in the process simulator PROSIM® [7], the simulation results are now accepted by the State of Texas for glycol unit permitting purposes. The only required analysis for BTEX is of the inlet gas as opposed to the expensive emissions testing of each glycol unit that had to be performed before reliable data were available.

There are numerous examples of the benefit of GPA funded research allowing more accurate glycol-BTEX predictions. At one time, it was believed that heating the rich glycol to 200°F would be sufficient to drive off the BTEX at the flash tank stage. Experimental data, incorporated into PROSIM, revealed that this approach would not be feasible [8]. However, the use of stripping gas in a secondary rich glycol stripping column was shown to perform satisfactorily both in simulation and in practice [9]. Significant savings were realized due to accurate predictions by the simulator since schemes for limiting BTEX emissions could be tested for feasibility before being implemented.

A related cost-saving benefit stems from the fact that glycol circulation rate can be optimized to maximize dew point depression while minimizing BTEX pickup and energy consumption by use of a simulator. In the past, more glycol than may have been necessary was circulated to ensure the lowest dew point depression without regard to the fact that BTEX pickup by glycols is proportional to the circulation rate. The simulator, with accurate BTEX pickup predictions attributable to GP A data, is able to predict the lowest circulation rate which allows the water specification to be satisfied while significantly reducing BTEX emissions in the still vent.

Yet another significant contribution of research by the GP A is in methanolhydrocarbon system VLLE. Before reliable methanol data were available, simulation predicted an excessive amount of methanol lost to the hydrocarbon phase, and less hydrate point depression than observed in an actual situation. This inaccuracy resulted in higher than necessary methanol usage. Figures 2-5 illustrate the improvement in methanol K values in PROS 1M due to the data contained in Research Reports 117 [10] and 149 [11]. The K value in these figures is defined as the mole fraction methanol in the vapor phase/mole fraction methanol in hydrocarbon liquid phase. Before incorporation of GP A data, results were off by at least one order of magnitude.

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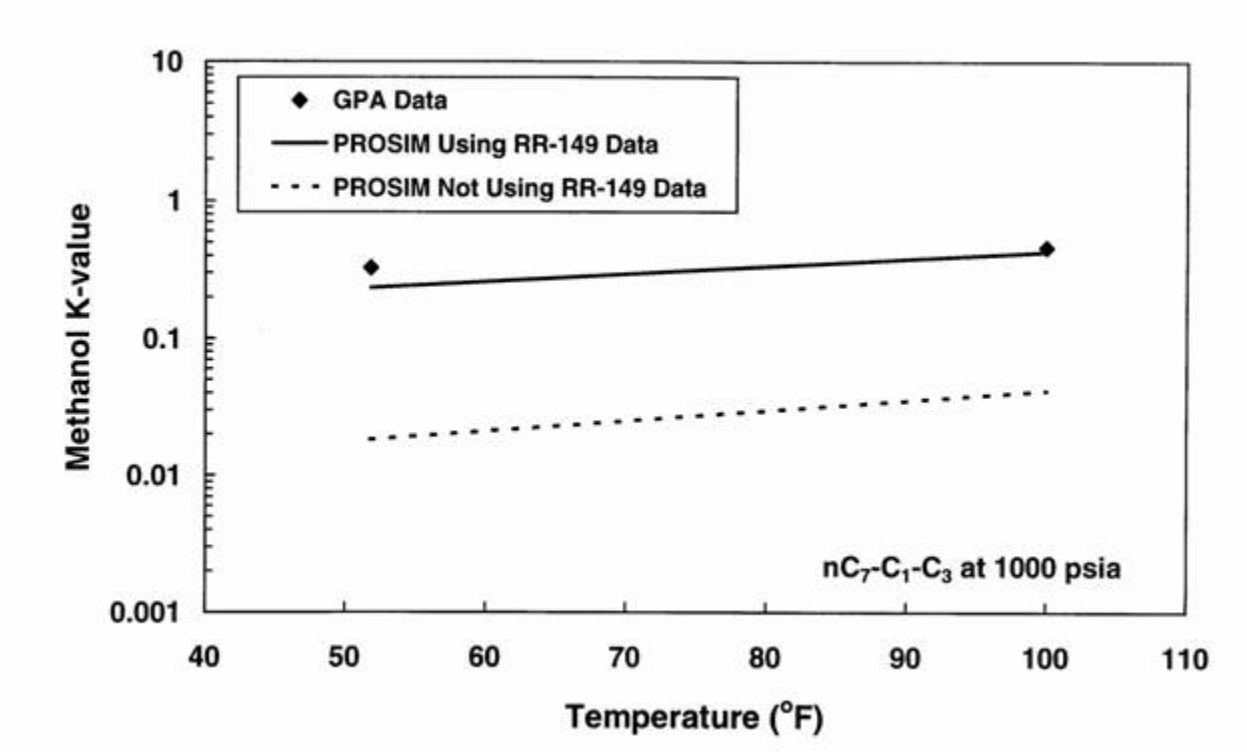

Figure 2. Methanol K-value improvement using RR-149 data for 25 wt% methanol

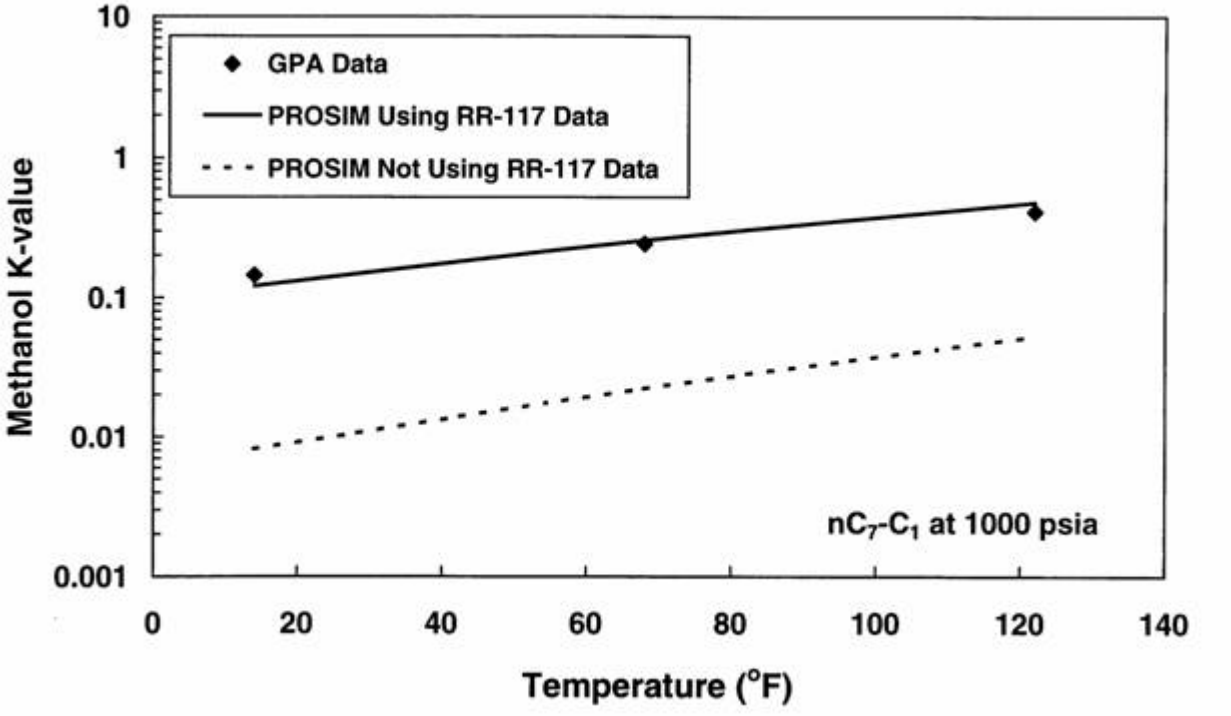

Figure 3. Methanol K-value improvement using RR-149 data for 50 wt% methanol

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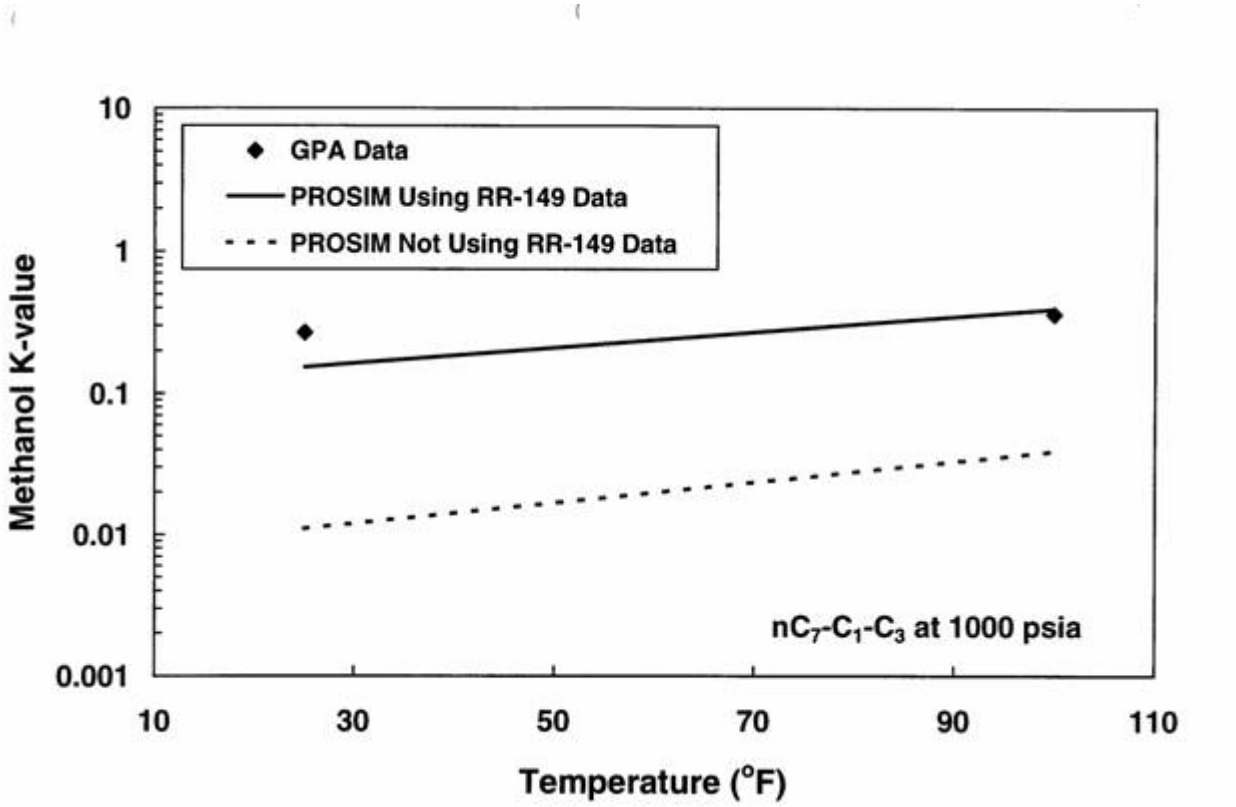

Figure 4. Methanol K-value improvement using RR-117 data for 35 wt% methanol.

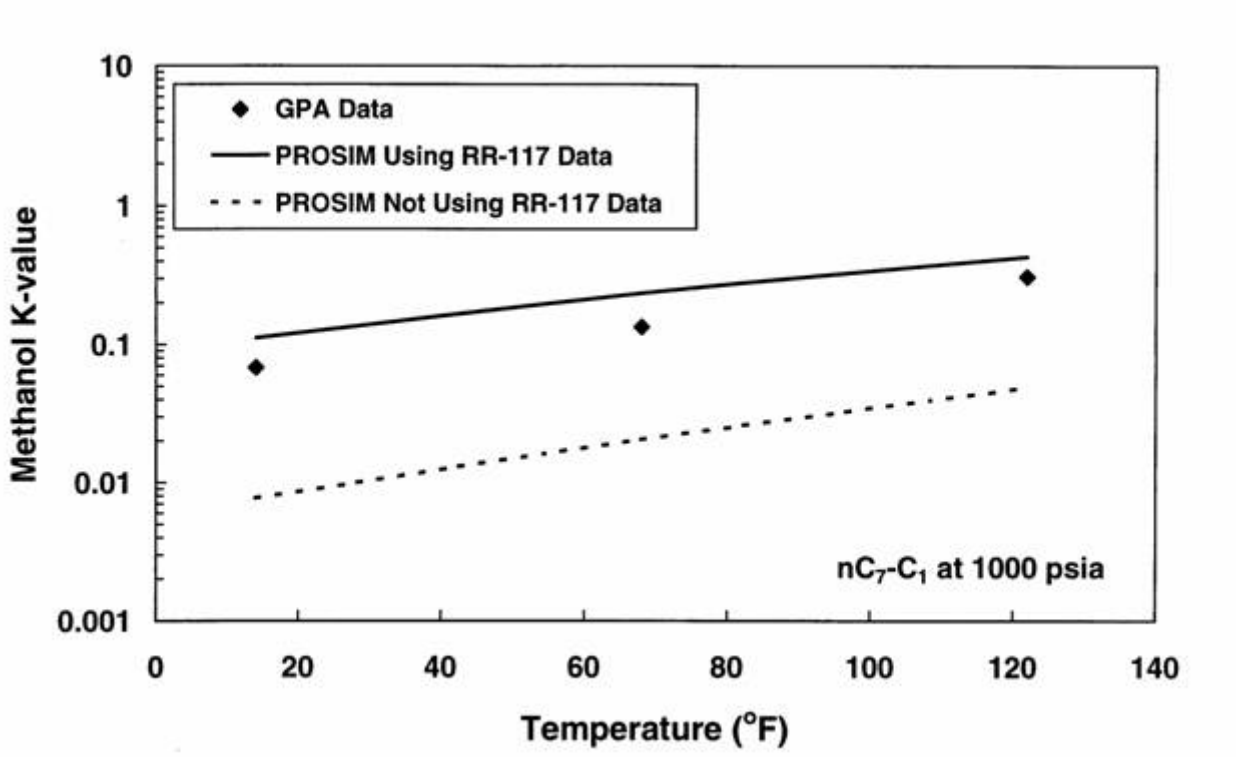

Figure 5. Methanol K-value improvement using RR-117 data for 70 wt% methanol.

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An example where data have improved the reliability of predictions is in hydrate formation temperature in the presence of inhibitors. The Hammerschmidt correlation can provide a reasonably accurate estimate of dew point depression at less than 20 weight % methanol in the aqueous phase and for lighter gases [12]. For higher weight % methanol or gases containing significant amounts of propane and heavier, the correlation is not as reliable. Although correlations have been developed which are valid for a wider range of inhibitor concentrations, the experimental data allow fine tuning of computation methods for extrapolation of data, which cannot be performed by empirical correlations.

Acid Gas Removal

Unlike hydrocarbon systems, amine system predictions in the liquid phase are typically based on activity coefficient models (Gibbs Excess Energy). Due to the chemical reactions involved and the ionic species present, the processes are much more complicated and difficult to predict than hydrocarbon systems. Accurate predictions require an enormous collection of data over a wide range of conditions. This range encompasses conditions at the absorber as well as conditions at the regenerator.

One example of the contribution of research data for acid gas solubility in amines concerns selective sweetening and amine choice. Prior to the 1980's, MEA and DEA, which readily absorb CO_2 along with H_2S, were used exclusively for sour gas sweetening. During the 1980' s, it was discovered that under certain conditions, the use of tertiary amines such as TEA and MDEA could improve sweetening plant operations by rejecting some of the CO_2 into the sweet gas [13]. By selectively absorbing H_2S from sour gas, the use of tertiary amines could allow a decrease in sweetening unit operating costs, not to mention improved feed quality to the Claus unit and decreased capital costs. The current trend is to find ways to increase selectivity to an even higher level (eg. colder temperature sweetening or new, more selective solvents). In order to accurately predict the CO_2-tertiary amine reaction, comprehensive data must be available. The research performed under GP A direction confirms previous data by others and supplies data unavailable elsewhere.

Table II illustrates how selective sweetening can make a substantial difference in amine unit efficiency. Because MDEA allows CO_2 to slip, a much lower circulation rate may be used as compared with MEA and DEA solutions. Since the size of the amine unit except for the absorber is directly proportional to the circulation rate, the lower circulation rate represents a reduction in both operating and capital costs. The following table provides a comparison of three amine solutions for treating a sour gas stream containing 100 ppm H_2S and 3 mole % CO_2 at a pressure of 800 psia. The results were generated using the process simulator TSWEET® [14]. (An H_2S specification of 4 ppm could be achieved with lower circulation rates for MEA and DEA, however, the rich loading would exceed 0.4.) Without accurate data, these results and comparison would not be possible as a practical matter.

Table II
Amine Solution Comparison

Amine	Weight %	Circulation Rate, gpm	H_2S in Treated Gas, ppm	CO_2 in Treated Gas, Mole %	Rich Loading, mol/mol
MEA	18	115	0.001	0.004	0.4
DEA	35	75	0.003	0.006	0.4
MDEA	45	40	0.13	2.0	0.2

FUTURE RESEARCH

As has been the case with past research funded by GP A, future research should lead to innovations that improve process economics through new processes or better designs of existing processes, improve operational safety, or address environmental concerns in the gas processing industry. The direction of the research will be determined by design, optimization, environmental, and legislative issues. The likely trend will be that many process design innovations will be driven by suppliers trying to obtain a competitive advantage. However, without basic data and

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research, much of the information leading to these design advancements will be unavailable.

The public perception of the gas processing industry should be the same as its perception of the electronics industry---an industry constantly searching for technological advances and improvements. Today, GPA sponsored research is critical due to decreasing research budgets in most companies, and the elimination of many research centers. Without research, the industry cannot progress. Failure to seek out technological advancements ensures that none will be found. The following list presents areas of possible future research consideration (some of these projects are currently under investigation):

Hydrocarbon Thermodynamics

1. Thermodynamic, transport, and hydrate property data for hydrocarbon systems at high pressure (>2000 psia), including systems that contain H_2S, CO_2, organic sulfur, methanol, glycols, and water.

2. Organic sulfur distribution in liquid hydrocarbons.

3. Fundamental research leading to novel thermodynamic and transport property models to improve engineering predictions.

Water Removal

1. Organic sulfur solubility in glycols and methanol.

2. Hydrocarbon solubility and other dehydration data for tetraethylene glycol or environmentally safe glycols such as propylene glycol.

3. Methanol-hydrocarbon VLLE over an extended range of temperature and composition, especially at lower temperatures.

4. Hydrate formation predictions and VLLE for systems containing *both* methanol and glycol.

Acid Gas Removal

1. Organic sulfur solubility in MEA, DGA and other systems to extend the recently completed Research Report RR-164 containing organic sulfur solubility in MDEA and DEA [15].

2. BTEX solubility in amine solutions.

3. Hydrocarbon solubility in loaded amine solutions, and solubility of amines in liquid hydrocarbons.

4. New solvents for improved performance in sour gas and LPG sweetening.

5. Effects of amine additives (e.g. acid buffers) and heat stable salts.

6. More extensive data for transport properties of loaded amine solutions.

7. Solubility of H_2S and CO_2 in amines at temperatures below 75°F (to maximize the selectivity of tertiary amines such as MDEA).

8. Refinement of measurements for acid gas partial pressure at low amine loadings to minimize the extremely large scatter in current data.

9. Data related to LPG treating.

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Miscellaneous Design and Optimization

1. Sulfur recovery methods alternative to the Claus process, such as liquid redox type reactions and direct oxidation.

2. Extension and refinement of properties of liquid sulfur containing dissolved H_2S.

3. Treating for contaminants other than H_2S and CO_2 (e.g. chlorinated hydrocarbons present in landfill gas).

SUMMARY

Through the years, GPA research has been directed toward custody transfer, phase separation, and contaminant removal. Most research is motivated by application of current technology. Some research is a direct result of legislative action. The objective of the research is to provide a set of quality data for use by the gas processing industry. Due to the widespread use of computers as an engineering tool, a majority of the research data is available in process simulation software. After incorporation into a simulator, the data can be used to optimize or improve engineering designs. If the past is any indication of the future, the gas processing industry can look forward to the continuation of quality research funded by GPA.

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