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BASIC DATA AND PHASE BEHAVIOUR METHODS

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1. INTRODUCTION

1.1 SCOPE

This is a new DEP which provides users of process, production and reservoir simulation programs with guidance on the application of basic data and the physical property predictive routines contained therein.

It provides an overview of the major predictive methods complete with a list of programs in which they are utilised. For each, there is a brief description and a discussion on areas of applicability and recommended applications.

In this DEP, reference is made to proprietary computer packages. Other packages with the same or similar functionality are available and may be used with the agreement of the Principal.

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1.3 DEFINITIONS

1.3.1 General definitions

The **Contractor** is the party which carries out all or part of the design, engineering, procurement, construction, commissioning or management of a project or operation of a facility. The Principal may undertake all or part of the duties of the Contractor.

The **Principal** is the party which initiates the project and ultimately pays for its design and construction. The Principal will generally specify the technical requirements. The Principal may also include an agent or consultant authorised to act for, and on behalf of, the Principal.

The word **shall** indicates a requirement.

The word **should** indicates a recommendation.

1.4 ABBREVIATIONS

EP - Exploration and Production (a Function in SIPM and the Royal Dutch/Shell Group)
EOS - Equation of State
KSLA - Koninklijke/Shell-Laboratorium, Amsterdam
KSEPL - Koninklijke/Shell Exploratie en Produktie Laboratorium
MF - Manufacturing (a Function in SIPM and the Royal Dutch/Shell Group)
MW - Molecular weight
PVT - Pressure, Volume and Temperature
VLE - Vapour - Liquid Equilibria
VLLE - Vapour - Liquid - Liquid Equilibria

1.5 CROSS-REFERENCES

Where cross-references to other parts of this DEP are made, the referenced section number is shown in brackets.

The documents listed in the bibliographies are for information only and do not form an integral part of this DEP. The Shell Group documents cannot be made available without express approval of the Principal.

2. GLOSSARY OF TERMS

Basic Data: This comprises all elements, data as well as programs, which are required to describe and predict the phase behaviour and physical properties of chemical mixtures at any specific condition.

Binary interaction coefficient: A constant which accounts for the deviation from ideality for two component mixtures. These are specific to one equation of state as they are calculated by regression of measured data. For example, those coefficients used in SMIRK (5.2.1) are quite different from those used in SRK (5.2.5), both in value and number.

The coefficients used in a liquid activity method are essentially regression constants used to calculate the liquid activity coefficient.

Dalton's Law: The pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the component gases.

Equilibrium coefficient or K value: This coefficient or ratio describes the distribution of a component between phases and is the keystone of all phase calculations. The higher the value the more volatile the component. A simple concept but a complicated function of pressure, temperature and composition.

Equation of state: An equation which describes the relationship between pressure, temperature and molar volume for any homogeneous fluid at equilibrium.

Fugacity: Translated literally it means escaping tendency and is an indication of the ability of a component to move between phases. At equilibrium, the fugacities of all phases are equal. For ideal gases where intermolecular interaction is, by definition, negligible, the fugacity and partial pressure of a component are identical.

Henry's Law: The partial pressure developed by a solute in a solvent is directly proportional to the mole fraction of the solute in the solvent. This is only true for low concentrations of solute.

Ideal gas: An ideal gas is one where the volume occupied by the molecules is infinitesimal when compared to the total volume occupied by the gas, i.e. the intermolecular force of attraction approaches zero.

Liquid activity coefficient: The ratio of the fugacity of a component in a mixture and in its pure state, at the same physical conditions, divided by its mole fraction in the mixture.

Parachor: A parameter describing the influence that a density difference between phases has on surface tension.

Principle of corresponding states: All gases when compared at the same reduced temperature and pressure have approximately the same compressibility factor and all deviate from ideality to the same degree.

Raoult's Law: The vapour pressure exerted by a component in ideal solution condition is directly proportional to its mole fraction.

3. COMPUTER PROGRAMS

Listed below are the various programs used within the EP function which utilise basic data.

3.1 SHELL

ASPHALT: A simple phase behaviour program for calculating asphaltene equilibria in reservoir fluids. Developed by KSEPL.

BOSIM/EOSIM: Non-compositional (black oil/volatile oil) and compositional reservoir simulators respectively.

C7PLUS: Converts the reported heavy end fraction of a hydrocarbon stream into a number of pseudo-components. The split is then tuned to match laboratory PVT data or well test results.

GAS FIELD PLANNING TOOL: An amalgamation of BOSIM and PIPEPHASE designed to allow optimum development and utilisation of gas reservoirs. A non-compositional simulator.

HERCULES: Hydrate prediction program. It uses a five phase flash routine developed by KSEPL to predict component distribution. KSLA are currently working on a replacement program due for end of 1993.

PVTPACK: A general purpose physical properties and phase behaviour package for use in reservoir engineering. It contains its own heavy end splitter routine, various equations of state and databases.

SHAMROCK: A general purpose phase behaviour simulation program developed and supported solely by MF. It has limited flowsheeting capabilities.This has now been deleted from the EAS (Engineering Analysis Suite) as its functionality is eclipsed by PROCESS and PRO/II.

SMBP: Shell Model Building Program. This is the Manufacturing (MF) developed and recommended flowsheeting program.

TEMPEST: A program for calculating well temperature and pressure profiles in production, injection and gas lifted wells. It is different from WIPCOG in that it looks at the transfer of heat from the fluid to the various casings and into the formation. It uses PVTPACK to generate physical properties and phase behaviour data but it is a non-compositional simulator.

TWOPHASE: Two phase flow simulator which uses the Shell basic data set and the KSLA pressure drop model. For use on single pipeline systems but not networks.

VLEOS: KSLA's flash and test program utilising the Shell basic data package.

WIPCOG: Well Intake Pressure Curves for Oil and Gas wells, is used for the prediction of pressure drops in production and injection strings and flowlines. It generates its own physical properties and phase behaviour data using an equation of state.

3.2 COMMERCIAL

NOTE: The definition of the word commercial as used in this manual, applies to software and technical data which is available from companies outside the Shell group.

Aspen Tech ASPEN+: A process flowsheeting program used by Chemicals Manufacturing (CMF). There is a Shell version which includes the KSLA basic data package but the contents of ASPEN+ are not covered by this manual.

PVTx: A heavy ends characterisation package used to split the C7+ fraction and assign physical properties. This program is still under evaluation by KSEPL but is available on the Wythenshawe Cray.

SimSci PIPEPHASE: This is a versatile multi-phase pipeline network simulation package which includes descriptions of well performance and simple processing facilities. There is a Shell version, PPHASE 601S, which includes the KSLA pressure drop model but not the Shell basic data package.

SimSci PRO/II: This is SimSci's major upgrade to PROCESS and will eventually replace it as the EP standard. A Shell version, PRO/IIS, was released in September 1991 which contains the Shell basic data package and the KSLA pressure drop and liquid holdup models and the C7PLUS heavy end splitter routine.

SimSci PROCESS: This is the standard EP steady state process flowsheeting program. In March 1990, a Shell version, PRO401S, was released which included the Shell basic data package and KSLA pressure drop and liquid holdup models.

4. THERMODYNAMIC BACKGROUND

In order to understand the differences between phase prediction methods, it is necessary to discuss how the various equations were developed and improved upon. This section provides a high level discussion of thermodynamic routines only. Should more detailed information be required, the documents listed in (4.2) should be consulted.

4.1 EQUATIONS OF STATE

The first scientific step to develop an equation of state was taken by Boyle in 1662. He proposed that a volume, V, of any gas at constant temperature was inversely proportional to its pressure, P.

$$PV = k \qquad (k=\text{constant})$$

In 1717, Charles discovered that, at a constant pressure, the volume of any gas was directly proportional to its absolute temperature, T.

$$V = kT \qquad (k=\text{constant})$$

These two gas laws were subsequently combined to create the ideal gas law:

$$PV = RT$$

where R was the universal gas constant, determined by experimentation and had the same value for one mole of any gas.

It was already known that this law was only applicable for ideal gases, hence its name, and that it had other faults such as its inability to predict the formation of liquids.

To account for non-ideal gases, the ideal gas law was modified using a compressibility factor, Z

$$PV = ZRT$$

This only accounts for some deviation from ideality but in real gases molecular attractions and repulsions do exist and exert a significant influence on the observed behaviour. This phenomena was investigated by van der Waals and the result of his work, published in 1873, was the first equation of state.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

where a and b are positive constants characteristic of a particular gas.

The term a/V^2 was intended to account for the forces of attraction which make the pressure lower than would be exerted by an ideal gas. Similarly, the b term was to account for the finite size of molecules which makes the volume larger than that for an ideal gas. The constants a and b can be determined by regressing experimental PVT data onto the equation. Setting the constants to zero reduces the equation back to the ideal gas law.

Mixtures were also described by van der Waals using the same equation but with the a and b parameters replaced by two new parameters, a_m and b_m, which described the behaviour of the mixture. These new parameters were determined using "mixing rules":

$$a_m = \Sigma\Sigma\, x_i x_j (a_i a_j)^{0.5}$$

$$b_m = \Sigma\Sigma\, x_i x_j (b_i b_j)/2$$

where a_i, a_j, b_i and b_j are the corresponding parameters for components i and j respectively.

Van der Waals is the simplest example of an equation of state and is known as a cubic, two parameter equation, as it is cubic when written with respect to volume with two adjustable constants. The majority of the equations of state used in EP phase behaviour programs are derived from this equation.

The van der Waals equation describes the coexistence of liquid and gaseous phases and also predicts the critical point, i.e. the point at which there is no difference between the two phases. However, its predictions are quantitatively poor and considerable efforts have been made to improve it in order to apply it with greater confidence.

The first significant improvement was made by Redlich and Kwong in 1949. Their equation of state, known as RK, was defined as:

$$P = \frac{RT}{V\ \ b} - \frac{a}{V(V-b)T^{0.5}}$$

Their improvement was to reproduce the fact that molar liquid volumes reduce at high pressures and that a better fit could be obtained by replacing the V^2 term by $V(V+b)$.

As the critical point is well defined, it is possible to express the *a* and *b* parameters in terms of the critical conditions. However, this approach implies that the critical compressibility is constant at 0.333 whereas experiments show that it can vary between 0.22 for C20 to 0.29 for C1 so limiting its accuracy close to the critical point.

The primary failure of the RK equation is its inability to accurately predict liquid densities (20 percent too low). This is because the *a* and *b* parameters are calculated using vapour pressure data only.

To allow the RK equation to be applied to more complex materials, Soave decided that the *a* parameter should be both temperature and material dependent. This additional dependency helps maintain the principle of corresponding states and is known as the Pitzer acentric factor, ϖ. This takes into account the departure from simple spherical molecules.

Soave's equation or SRK, proposed in 1972, is written as:

$$P = \frac{RT}{V-b} - \frac{a_t}{V(V+b)}$$

where a_t is the temperature and composition dependent *a* parameter which is defined by the critical pressure and temperature and the acentric factor. At the critical point, the *a* parameter for SRK and RK is equal. The *b* parameter remained independent of temperature and identical to that used in RK.

To allow the equation to accurately predict the phase behaviour of mixtures of dissimilar components, e.g. methane and nitrogen, binary interaction coefficients, K_{ij}, were introduced. These were used to modify the *a* parameter mixing rule to take into account weak molecular interactions. The mixing rule then became:

$$a_m = \sum\sum x_i x_j (a_i a_j)^{0.5} (1-K_{ij})$$

This equation still gave poor predictions of liquid density as the constants were derived from vapour pressure data between a reduced temperature of 0.7 and the critical point.

Peng and Robinson (1976) used a slightly different *a* parameter from SRK as they used vapour pressure data from the normal boiling point to the critical point. They also used a slightly different volume dependence and thus obtained a lower value for critical compressibility, 0.307. Their equation, PR, is written as:

$$P = \frac{RT}{(V-b)} - \frac{a_t}{V(V+b)+b(V-b)}$$

This did not greatly improve liquid density prediction but did improve accuracy for heavier hydrocarbons above C5. The equation underpredicts by 5-10 percent the density for light hydrocarbons, C1-C5 and overpredicts for heavier ones.

To overcome the problem of liquid density prediction, KSLA proposed that the *b* parameter should also be temperature dependent. The *a* and *b* parameters were not derived from the critical conditions but fitted to both liquid density and vapour pressure data. Their equation, known as SMIRK (Shell Modified and Improved Redlich-Kwong), is defined as:

$$P = \frac{RT}{V - b_t} \quad \frac{a_t}{V(V + b_t)}$$

SMIRK has similar inaccuracies as SRK and PR close to the critical point and when differentiated to give enthalpy there is a discontinuity which has to be smoothed out. In general, it overpredicts both critical pressure and volume by 10 percent but vapour pressure and liquid density are within 1 percent. The equation also includes a modification to the *b* parameter mixing rule to allow for the use of interaction coefficients.

For mixtures of polar and non-polar components, the modified van der Waals mixing rules are insufficient. For example, they cannot replicate the fact that the solubility of water in oil is far greater than the reverse. This irregularity is due to the asymmetry in the intermolecular attractions. For such systems, asymmetric mixing rules are introduced which modify the binary interaction coefficient to take into account the concentration of each component.

$$K_{ij} = K_{ij}^{o} + (x_i - x_j)\, K_{ij}^{1}$$

Hence, two coefficients K_{ij}^{o} and K_{ij}^{1} are required for each binary.

All coefficients are determined by regression of experimental data for binary systems and then applied to multicomponent mixtures.

The inherent limitations of the cubic equations of state can only be overcome by equations which are necessarily more complex. The Benedict-Webb-Ruben equation contains eight adjustable parameters but is still only accurate for pure components or similar component mixtures. Their equation, BWR, is written as:

$$P = RT / V + (B_o RT - A_o - C_o / T^2) / V^2 + (bRT - a) / V^3$$

$$+ a a / V^6 + (C / V^3 T^2)(1 + g / V^2) \exp(- g / V^2)$$

where A_o, B_o, C_o, *a*, *b*, *c*, *a* and *g* are constants for a particular fluid.

4.2 LIQUID ACTIVITY METHODS

For any component in a mixture, a state of equilibrium exists when the fugacity, *f*, of the liquid and vapour phases is equal, i.e.:

$$f_i^v = f_i^l$$

In the vapour phase, the fugacity depends on the system pressure, *P*, temperature and mole fraction, *y*. They can be related using the vapour phase fugacity coefficient, *f*:

$$f_i^v = P f_i y_i$$

For an ideal gas, f_i =1 and as the pressure approaches zero, f_i, approaches unity. However, it is a false assumption to assume that when the pressure is low, f_i is unity.

The liquid phase fugacity is related to the mole fraction, *x*, through the liquid activity coefficient, *g*:

$$f_i^l = g_i x_i f_i^o$$

where f_i^o is the standard state fugacity of the liquid at the system pressure and temperature.

Combining the two equations:

$$K_i P f_i = g_i f_i^o$$

This equation is used by all the liquid activity (LACT) methods to calculate K values.

The vapour phase fugacity coefficient, f_i, is calculated using any equation of state, SRK, RK, PR or SMIRK.

Standard state fugacity, f_i^o is calculated from:

$$f_i^o \ z = P_i^o \ v_i^o \ \exp\left[(P - P_i^o)\frac{\rho}{RT}\right]$$

where

v_i^o	is the pure component fugacity coefficient.
P_i^o	is the component vapour pressure
R	is the universal gas constant
ρ	is the liquid density.
T	is the system temperature
P	system pressure

v_i^o is calculated from the equation of state and the remaining items are held in the pure component database.

The activity coefficients are generated by various methods from binary interaction data.This data is different to that used in equations of state to account for deviation from ideality (4.1). Typical methods available to EP users are UNIFAC (5.3.3) and NRTL (5.3.2).

This approach is normally used for liquid-liquid systems but can be applied to vapour-liquid systems.

Bibliography:

"Properties of Gases and Liquids" 4th Edition. Reid, Prausnitz and Poling.

"Properties of Oils and Natural Gases" 1st Edition. Pedersen, Fredenslund and Thomassen. Gulf Publishing Company.

Journal Pet Tech, April 1988 p 397. A. Firoozabadi "Reservoir- Fluid Phase Behaviour and Volumetric Prediction with Equations of State".

R. Reijnhart, J. de Dood and H. Meijer. "The use of equations of state in the Petrochemical industry"(1986).

"Gas Conditioning and Processing. Vol I". J.M. Campbell.

5. PHASE BEHAVIOUR PREDICTION

In this section, the relative merits of the various predictive equations are discussed. The section is split into four parts:

(5.1) contains those equations which calculate K values only.
(5.2) has the more complex equations of state which provide various other physical properties as well as K values.
(5.3) discusses liquid activity methods.
(5.4) provides an overview of the black oil correlations used in non-compositional simulators.

Appendix 7 shows the availability matrix of phase behaviour models and simulation programs.

NOTE: When discussing SimSci programs, the term (S) after the program name refers to the Shell version only. Otherwise any comments apply to both versions.

5.1 IDEAL METHODS

Ideal Methods ignore any non-ideal behaviour. In the case of gases they assume that the ideal gas law applies and for liquids they assume that the partial molar volume of a component in a mixture is equal to the molar volume of the pure component. These restrictions severely limit their applicability, but despite this they still form a useful addition to any simulation program.

5.1.1 Shell standard oil system, STND

Available: SHAMROCK, SMBP, PROCESS(S), PRO/II(S)

Description:The effect of pressure on fugacity is neglected in STND and only Raoult's law is applied. Depending on the boiling point of the component and the stream temperature, the routine selects one of five different methods to calculate vapour pressure or interpolates between two. There are separate correlations available for light hydrocarbons with nitrogen and hydrogen.

Validity: Pressures below 500 kPa, moderate temperatures (273-573 K), non-polar compounds and water. Maximum carbon number is 100. Each correlation has its own validity range. This method calculates only K values and enthalpies, different methods are required for phase densities and entropy.

Application: Oil fractions or for systems where sharp separations are not required. Primarily used in MF.

Key points: Water is automatically decanted once its solubility in the oil phase has been calculated using standard kerosene/water data.

Bibliography:

MF 85-1250 ."User manual for new SHAMROCK flash program". Appendix 8.3.

SimSci PRO/II INPUT Manual. Shell addendum May 1991.

5.1.2 Braun, K10

Available: PROCESS, PRO/II, PIPEPHASE

Description: A vapour phase correlation which ignores non-ideality due to pressure. It uses the same technique as STND (5.1.1).

Validity: Pressures below 700 kPa and temperatures between 313- 473 K.

Applications: Ideal for vacuum columns.

Key points: It calculates K values only, therefore alternative methods are required for enthalpy, entropy and density. It cannot handle water rigorously.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.1.3 Grayson Streed, GS

Available: PROCESS, PRO/II, PIPEPHASE

Description: This method uses the RK equation of state to calculate the vapour phase fugacity coefficient and the regular solution theory to calculate the liquid activity coefficients. To improve its accuracy, correlations for vapour phase fugacity are available but for C1-C8 only.

Validity: Temperatures between 253 to 723 K, pressures below 20 000 kPa and for fluids with less than 5 percent inerts.

Applications: Primarily for MF type applications such as crude towers but suitable for light hydrocarbon systems especially depropaniser and debutaniser columns. Superseded by SRK (5.2.5) but still used within MF.

Key points: This is a totally predictive routine which requires no pure component data. It was developed for high temperature, high hydrogen content streams found in refineries. It calculates K values only so alternative methods are required for enthalpy, entropy and density. It cannot handle water rigorously.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.2 EQUATIONS OF STATE

5.2.1 Shell, SMIRK

Available: PROCESS(S), PRO/II(S), PVTPACK, TWOPHASE, WIPCOG, SHAMROCK, SMBP, VLEOS, ASPEN+

Description: A modified Redlich Kwong equation of state developed by KSLA (4.1). The temperature coefficients of the *a* and *b* parameters have been regressed from liquid density and vapour pressure data to overcome the limitations of other RK based equations. The coefficients are available for all pure components in the Shell physical property data base, PEPPER (6.1.1).

Validity: Not as accurate near critical point (10 percent error) as SRK but very accurate prediction of liquid density. There are no limits on pressure and temperature applicability within normal EP operations.

Application: It is suitable for all hydrocarbon systems and simulates water-hydrocarbon and non-ideal systems with good accuracy provided interaction coefficients are available. It will work in VLE as well as VLLE mode but it is not as accurate as NRTL (5.3.1) for low pressure liquid-liquid systems.

Key points: Use of SMIRK allows a consistent and rigourous thermodynamic method to be used across all Shell programs. Good interaction coefficient data base although the data for glycols and oil in water should be used with caution as they are based on limited data (Appendices 1, 2 and 5). A new mixing rule has recently been introduced to eliminate the "isomer paradox" (see AMGR 91.143) but this has not yet been released from KSLA. The paradox occurs when a stream contains many isomers and the mixing rule, when expanded, creates interactions which do not occur in reality.

Bibliography:

AMGR 82.194 & 82.195 J de Dood and P.Heijink. "Development of the SMIRK82 Equation of State".

AMGR 91.143, E.M. Hendriks and A.J.M. Olijve. "Implementation of SMIRK Equation of State Mixing Rule".

EP 92-0665 W. Swinkles "Reservoir Engineering Guidelines for Gas Condensate Fields".

5.2.2 Shell modified Soave Redlich Kwong, MRKS1

Available: PVTPACK

Description: Developed by West Hollow Research Centre (WRC), Houston, it is a modified version of SRK but utilises improved mixing rules. KSEPL modified the equation to allow it to better predict the behaviour of components with a high acentric factor. A correlation is used to generate interaction coefficients or user supplied data can be input.

Validity: It cannot handle water and gives a poor prediction of liquid density. It will only use data from the PVTPACK database and therefore its results should be used with caution in other phase behaviour programs.

Application: Only for use with old, reservoir models.

Key points: Out of date. Superseded by MRKS2 (5.2.3) and SMIRK (5.2.1).

Bibliography:

WRC 75.24, P.L. Chueh and P.C. Samish. "Calculation of reservoir fluid behaviour.Computer program MRKS1".

EP 90-2325, A.R. van Bergen and K. van Leeuwen. "PVTPACK User Guide". Appendix A.

5.2.3 Shell modified Soave Redlich Kwong, MRKS2

Available: PVTPACK, HERCULES

Description: Developed by Shell Oil from MRKS1 by introducing new correlations (MRKS 2.6 and 2.10) for the interaction coefficients to improve predictions for systems containing water, hydrogen sulphide and carbon dioxide. It has the same acentric factor modification as MRKS1.

Validity: See (5.2.2). It will handle water but no other polar compounds. Suitable for light, C1 to C20, hydrocarbons only.

Application: Unsuitable for high temperatures and pressures close to the critical point or for mixtures with high concentrations of inerts, e.g. nitrogen, carbon dioxide, etc. The user can specify which interaction parameter set to use. The selection of the set depends on how accurately the program matches known data.

Key points: Superseded by SMIRK (see EP 87097) but perfectly acceptable for use in Hercules with the usual caveat on liquid densities. Use of the BWRS equation of state (5.2.4) to calculate liquid density in place of MRKS is thermodynamically inconsistent as the correct model should describe both properties. However, the effect of this is unknown. HERCULES utilises the MRKS 2.6 interaction parameter set.

Bibliography:

EP 51527, J.F. Ely and P.L. Chueh. "Reservoir fluid phase equilibrium computer program MRKS2".

EP 87077, G.S. Shealy and V.L. Higgins. "SMIRK and MRKS2 equations of state.A fundamental comparison".

EP 90-2325, A.R. van Bergen and K. van Leeuwen. "PVTPACK User Guide". Appendix A.

EP 51101, R.B. de Boer. "HERCULES: A computer program for calculating hydrate expectancy regions".

5.2.4 Benedict Webb Rubin Starling, BWRS

Available: PVTPACK, PRO/II, PROCESS

Description: A complex equation of state which utilises 11 adjustable parameters per component. A non-cubic equation of state.

Validity: It is valid for the normal EP range of temperature and pressures. Suitable for non-polar mixtures only as it does not utilise interaction parameters.

Application: Its main use is to very accurately predict the properties of a single component.

It gives a good prediction of liquid density provided all the data is available. It cannot be used for rigorous three phase calculations, offering only simple water decant. Similar uses as SRK, i.e. light hydrocarbon systems.

Key points: Requires 11 items of data for each component. The version in PROCESS is a SimSci modified version of BWRS.

Bibliography:

J.Chem Phys 1940 vol 8, p334 M.Benedict et al. "An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures".

EP 90-2325, A.R. van Bergen and K. van Leeuwen. "PVTPACK User Guide". Appendix B.

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.2.5 Soave Redlich Kwong, SRK

Available: PROCESS, PRO/II, PIPEPHASE, ASPEN+

Description: See (4.1). Developed from data for methane to decane. Binary interaction data is available to account for non-polar and weak polar interactions (SimSci programs only). Correlations are used to generate binary data for pseudo-components.

Validity: Its accuracy decreases near the critical point but it gives an accurate prediction of the point itself. Liquid density prediction is very poor. The mixing rule is simple and therefore it cannot be used for polar compounds. It is valid for systems with less than 5 percent inerts over the full range of EP pressures and temperatures. Ideal for producing heat and mass balances where water phase accuracy is not essential.

Application: Light, C1-C10, hydrocarbons. Simple water handling capability. Not for polar components or for heavy components above C20.

Key points: Robust and well proven. Ideal for use in basic flowsheeting problems. At high pressures with a separate water phase present use SMIRK (5.2.1) or SRKKD (5.2.6). Liquid densities should always be calculated using a different method, see (7.2). When using PRO/II (pre version 3.1) select SIMSCI physical property database and not the default to ensure that all interaction coefficients are retrieved.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

SimSci PIPEPHASE input manual. Chapter 6, Rev. 4, July 1989.

5.2.6 SRK modified by Kabani - Danner, SRKKD

Available: PRO/II, PROCESS

Description: Modification of SRK specifically to predict VLLE data for hydrocarbon - water systems. An asymmetric mixing rule is used to take into account the water - hydrocarbon interactions, hence a new set of interaction coefficients are required for oil in water. The remaining binaries are as per SRK. These are available in the SimSci database (Appendix 3). For pseudo-component binaries, a set of correlations is used. Correlations are used to generate binary data for pseudo-components.

Validity: Same accuracy as SRK near the critical point and gives poor prediction of liquid densities. Not for use with strongly polar compounds other than water, e.g. methanol. A separate water phase must be present.

Application: Rigorous three phase flash calculations for systems with high concentrations of inerts at high pressures. Comparable with SMIRK for accuracy but for these systems only.

Key points: Check the list of binaries called from the database to ensure that there are no gaps. When using PRO/II, pre version 3.1, select the SIMSCI physical property database and not the default. See (6.2). Developed specifically for water-hydrocarbon systems.

Liquid densities should always be calculated by an alternative method. See (7.2).

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.2.7 SRK modified by SimSci, SRKM

Available: PRO/II.

Description: A SimSci modification to the SRK mixing rule to allow modelling of polar and non-polar systems. Four sets of interaction coefficients are required which are available in the SimSci database. If there are no SRKM binaries, the system will default to SRK binaries and then to ideal. Correlations are used to generate binary data for pseudo-components.

Validity: For the normal range of EP pressures and temperatures. A greater number of binaries are available than for SMIRK (Appendix 4) and are produced from more data. Prediction of liquid densities is poor. There is some doubt over the validity of the mixing rule when dealing with isomers: the so-called "isomer paradox". This was first identified in SMIRK and has subsequently been corrected. Its appearance in SRKM has been investigated and will be corrected in versions after 3.1.

Application: As for SRKKD but better suited for polar/non-polar systems. It can be used to model glycol systems, water - methanol - hydrocarbon systems and sour water systems with less than 30 mol percent sour components.

Key points: Check that the list of binary data called from the database has no gaps. There is limited data available for glycol systems and due to a bug, not all of this data is retrieved from the database and it has to be input manually. This problem has been corrected in version 3.1. An alternative method must always be used to calculate liquid densities. See (7.2).

Bibliography:

SimSci PRO/II Input Manual, February 1991.

5.2.8 Peng-Robinson, PR

Available: PROCESS, PRO/II, PVTPACK, PIPEPHASE, HERCULES

Description: Another modification of the van der Waals equation aimed at improving liquid density prediction. See (4.1).

Validity: Same as SRK (5.2.5) but has greater accuracy near the critical point. Prediction of liquid density is better than any SRK derivatives, with the exception of SMIRK, none the less it is still poor.

Application: As SRK. See (5.2.5).

Key points: Robust and well proven. Ideal for simple heat and mass balances but liquid density should always be calculated by a different method (7.2).

The version used in PVTPACK and HERCULES utilises a unique database (6.1.4) and separate values, in the form of correlations, for interaction coefficients. It also utilises the KSEPL modification to allow for components with high acentric factors.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

EP 90-2325, A.R. van Bergen and K. van Leeuwen. "PVTPACK User Guide". Appendix B.

RKGR.79.052, R.B.de Boer. "HERCULES: A computer program for calculating hydrate expectancy regions".

5.3 LIQUID ACTIVITY METHODS

5.3.1 Shell Non-random two liquid method, SNRTL

Available: PROCESS(S), PRO/II(S), SMBP, VLEOS, SHAMROCK, ASPEN+

Description: The NRTL equation uses binary interaction data to calculate liquid activity coefficients and hence K values (4.2). It also uses SMIRK to calculate the vapour phase fugacity coefficients and liquid molar volumes. The remaining data, pure vapour pressures, etc., are retrieved from the Shell PEPPER database (6.1.1). User supplied binary data can also be used.

Validity: Interaction coefficients for all components must be available as there is no automatic fill-in method available (under development). This method should not be used if the temperature is above the critical temperature of one of the components. Pressures below 1500 kPa only.

Application: For PEPPER compounds only. For use in highly non-ideal systems and where very sharp separations are required. It is valid for both liquid - liquid and vapour - liquid - liquid systems and it is the preferred liquid activity method due to its flexibility. Excellent for azeotropic columns.

Key points: Care must be exercised when using this method to ensure uniformity of data. If there is no data available the routine assumes ideal behaviour. Do not extrapolate to pressures and/or temperatures above those at which the measurements were made as accuracy falls off quickly. It is not a method for the inexperienced user.

Bibliography:

A.I. Chem. E. Journal 1968 Vol 14 p135. J.M. Prausnitz and H. Renon. "Local composition in thermodynamic excess functions for liquid mixtures".

5.3.2 SimSci Non-random two liquid method, NRTL

Available: PROCESS, PRO/II

Description: As for the SNRTL (5.3.1) but any equation of state can be used to calculate the vapour phase fugacity coefficient. However, the best results will be obtained if the same equation is used as used to develop the interaction constants.

Validity: As for the SNRTL although the SimSci databases do not contain as many interaction coefficients as PEPPER (3000 against 5000). The method, as a default, assumes ideal behaviour in its calculation of enthalpy and density but any equation of state can be used.

Application: As for SNRTL (5.3.1).

Key points: Automatic fill-in option is available when interaction data are missing (5.3.3). Accurate liquid density data is essential. The PROCESS version uses six parameters whilst the PRO/II and Shell version utilises eight.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.3.3 Group contribution method, UNIFAC

Available: PROCESS, PRO/II

Description: This utilises existing phase equilibria data to predict phase data for systems where no such data is available. Basically, activity coefficients for mixtures are related to interactions between structural groups and corrections are then applied to take into account differences in molecule size and molecular interactions.

Validity: This is an approximate method only and should not be used for detailed design. It is not yet available for SNRTL but is under test at KSLA.

Application: For use when data are not available for the desired system and the effects of non-ideality cannot be ignored.

Key points: Works best at pressures below 500 kPa and temperatures between 300 K and 425 K.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.3.4 Henry's law

Available: PROCESS, PRO/II

Description: Combining Henry's and Dalton's laws, the equilibrium constant is shown to be inversely proportional to the system pressure. Hence, using only Henry's constants the composition of the phases can be determined.

Validity: A limited range of data is available and Henry's constants are strongly affected by temperature.Valid only at pressures below 500 kPa. For use with any liquid activity method. As a rough guide, if the solute concentration is above 100 ppm then the linear relationship is no longer valid.

Application: For determination of solubility of gases in liquids and for air stripping columns.

Key points: The gas phase must be non-condensible.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

5.4 BLACK OIL CORRELATIONS

Black oil correlations are used primarily in reservoir and two phase (PIPELINE) simulations as a means of reducing computation time. By definition the term "Black oil" refers to a set of multiphase fluid correlations which calculate the phase split and bulk fluid properties from the individual gas and liquid gravities and gas/oil ratio. For this assumption to be valid, the liquid must remain in the liquid phase at all times. The gas, however, can exist either in solution or as a separate phase. The simulation conditions should mirror the conditions at which the correlations were developed.

Each program utilises different correlations for generating solution gas/oil ratios or phase splits. A brief overview of those used in EP programs are given below. If further information is required, then the references for each program should be consulted.

5.4.1 SimSci PIPEPHASE

Description: Contains three correlations - Lasater, Standing and Vazquez - for the calculation of solution gas/oil ratio's.

Application: For use when rigorous modelling is not required and when the range of temperatures and pressures is within the range of applicability.

Validity: Not for light oils which may vaporise under reservoir conditions.

Bibliography:

SimSci PIPEPHASE input manual Chapter 33, Rev. 4, July 1989.

5.4.2 Shell TWOPHASE

Description: Solution gas/oil ratios are calculated using the Lasater, Standing and Katz correlations which can be modified for pressure. Temperature effects can also be allowed for if viscosity data is available at one or two temperature points.

Application: For use when rigorous modelling is not required and when the range of temperatures and pressures is within the range of applicability.

Validity: The program will provide warnings if any of the specified input data or results are out of range. For a full list of applicability ranges consult the referenced user guide.

Bibliography:

EP 89-1780 (AMGR 89.123). N. Trompe. "TWOPHASE User Guide".

5.4.3 Shell PVTPACK

Description: PVTPACK as such does not contain any black oil correlations. When creating input for BOSIM or TEMPEST, it converts data generated by an equation of state into curves of compressibility, formation volume factor and GOR against pressure.

Application: Suitable over the same range as the equation of state used to generate the data. A far more accurate method than simple correlations.

Validity: When creating input for EOSIM which only uses the RK equation, the MRKS2 equation should be used and not PR or SMIRK.

Bibliography:

EP 90-2325 A.R.van Bergen and K. van Leeuwen. "PVTPACK user guide".

6. PHYSICAL PROPERTY DATABASES

Each simulation program requires access to a large physical property database to obtain pure component and binary interaction data. The depth and accuracy of this data form the basis of a successful simulation and time spent ensuring that the data is correct is never wasted. The old adage of "Rubbish in = Rubbish out" is always true.

6.1 SHELL

The Shell databases were created to support Shell developed phase simulation programs. Whilst the data held in them may be the same in many instances they can only be used in conjunction with the programs specified.

6.1.1 PEPPER

Available: TWOPHASE, WIPCOG, PROCESS(S), PRO/II(S), SHAMROCK, PVTPACK, SMBP, VLEOS

Description: The Shell data base for pure component properties. It contains 975 components with over 60 data items on each, along with correlations for temperature dependent properties, i.e. heat of vaporisation.

Validity: For the full range of EP pressures and temperatures.

Application: Forms the basis of the Shell basic data package.

Key Points: The database is suitable for use with the Shell generated methods only.

Bibliography:

AMGR 85.232 J. de Dood, A.J.M. Olijve and C.L.M. Vrouwenvelder "PEPPER: A data base system for phase equilibria and physical properties of pure compounds and binary mixtures".

AMGR 90.352 J. de Dood and A.J.M. Olijve. "The PEPPER database status report 1989".

Booklet distributed by KSLA J de Dood and A.J.M. Olijve. "PEPPER component index". Issued 12 February 1990.

6.1.2 BEPPER

Available: With PEPPER

Description: The binary interaction coefficient data base for both SMIRK and SNRTL. Although this a discrete database, the whole system of data files, literature references, etc is called PEPPER. The binary interaction coefficient file, BEPPER, is only available within PEPPER.

Validity: Only a limited set of binary data for SMIRK is available (Appendix 5). There are generalised expressions for water, nitrogen, carbon dioxide, hydrogen, hydrogen sulphide and methanol with light, C1-C16, straight chain hydrocarbons and some aromatics. The data for MEG and DEG should be used with caution. See (Appendices 1 and 2).

Most of the polar/non-polar binaries were regressed with limited data (what was available at the time). Hence any results generated using these must be treated with care. An inventory of the BEPPER database has been completed which gives the pressure and temperature ranges for each binary (ST/138/92).

For the NRTL method there are over 5000 binary pairs available making it a powerful tool under the correct conditions (5.3.1).

Application: With SMIRK and SNRTL.

Key points: Contact KSLA if interaction coefficients are not available in PEPPER as there may be experimental data which has not yet been used to generate interaction coefficients.

Bibliography:

ST/138/92 J. de Dood. "Basic data for waste reduction: Inventory and recommendations for future work".

ST/096/91 J. de Dood. "Availability of binary interaction coefficients (SMIRK) and experimental data for waste prediction in gas processing operations".

6.1.3 PVTPACK (PEPPER)

Available: PVTPACK

Description: This is essentially a small portion of PEPPER containing only those components, 115 in total, required by the reservoir engineer.

Validity: Suitable for use by SMIRK only.

Application: As for PEPPER.

Key points: This separate database will soon be deleted and the new open systems version of PVTPACK will access the same database as other Shell programs.

Bibliography:

EP 90-2325 A.R. van Bergen and K. van Leeuwen. "PVTPACK user guide".

6.1.4 PVTPACK

Available: PVTPACK, HERCULES

Description: A data base set up by WRC to support their MRKS and PR equations of state. The data base contains pure component data for 68 compounds only. The interaction coefficients for use in those equations are generated using correlations.

Validity: This database supports the MRKS and PR equations of state in PVTPACK and HERCULES. SMIRK cannot utilise this data base. This database has not been updated since at least 1986 and may, therefore, be inaccurate. The range of components could affect its applicability in the user programs.

Application: If the MRKS or PR equations are used in PVTPACK or HERCULES this database has to be used. Due to its age it may not be as accurate as PEPPER but it should be bug free.

Key points: Old. Limited number of components.

Bibliography:

EP 51527 J.F. Ely and P.L. Chueh. "Reservoir fluid phase equilibrium computer program MRKS2".

6.1.5 STEAM

Available: PROCESS(S), PRO/II(S), TWOPHASE, SHAMROCK, SMBP

Description: Steam tables taken from the public domain with no modifications.

Validity: At high pressures with natural gas use tables developed by the GPSA.

Bibliography:

"Properties of water and steam in SI units". Prepared by E. Schmidt. Published by Springer Verlag 1982.

"GPSA engineering data book". 10th Edition 1987.

6.2 COMMERCIAL

The SimSci data base actually consists of five discrete databanks: "Process, Simsci, DIPPR, User and Electrolyte". Each one contains specific items of data which are required for a simulation. In the Shell versions of PROCESS and PRO/II, the user can also access PEPPER, BEPPER and STEAM.

Available: PROCESS, PRO/II, PIPEPHASE

Description: Contains the pure component data and temperature dependent correlations for over 1550 pure components. It also contains binary data for the several equations of state and LACT methods available to users. Access can also be made to the DIPPR database and SimSci's electrolyte database and specific user created databases.

Applicability: For use with all the SimSci equations.

Validity: For PROCESS before version 4.01 the database is different and consists of two separate banks called 'PROCESS' and 'NEWBANK'. The old 'PROCESS' database is different from that called 'PROCESS' in PRO/II.

Key points: It is possible to view the binary data being used in a simulation to ensure that there are no gaps. The default database is PROCESS which does not contain as many interaction coefficients as the SIMSCI database. Hence, interactions will be assumed to be ideal if no data are present. In versions after 3.1 SIMSCI is now the default.

7. LIQUID DENSITY METHODS

As discussed in (4.1), the ability of equations of state to accurately predict liquid densities varies widely. Accurate density data is essential, i.e. for constant volume depletion tests. Liquid density also provides the basic input into the NRTL equations (4.2) and in the calculation of viscosity and thermal conductivity (8.1 and 8.3).

7.1 SHELL

The Shell method for the prediction of liquid density is via SMIRK. The only exception to this rule is in PVTPACK where BWRS is used to overcome the inherent inaccuracies of the MRKS or PR equations. The latter is an accurate method but it cannot deal with water and some modification is required if measured densities are to be matched.

7.1.1 Shell SMIRK

Available: PVTPACK, SMBP, SHAMROCK, TWOPHASE, VLEOS, PROCESS(S), PRO/II(S), WIPCOG

Description: Utilises the SMIRK equation of state to predict liquid densities as the correlations used to calculate the *a* and *b* parameters were regressed from liquid density data.

Validity: Suitable for all components in EP operations both heavy and light and polar and non-polar. Accuracies to within one percent are common for similar mixtures. The accuracy reduces as the temperature rises towards the critical temperature.

Application: Suitable for all EP applications where accurate density predictions are required.

Key points: Only available with SMIRK and the PEPPER database.

Bibliography:

AMGR 82.194 & 82.195 J. de Dood and P. Heijink. "Development of the SMIRK82 equation of state".

7.2 COMMERCIAL

The SimSci packages contain a full range of liquid density methods and these are covered in their reference manuals. Only those recommended for use are discussed in this DEP.

7.2.1 API

Available: PROCESS, PRO/II, PIPEPHASE

Description: The method was developed from that used in the API technical data book.

Validity: Suitable for a wide range of light and heavy hydrocarbon mixtures providing the reduced temperature is below 0.95.

Application: For use with the SRK and PR equations in all their guises with the exception of SMIRK. Accuracies to within one percent are common. This reduces to approximately 15 percent close to the critical point.

Key points: Best for use with heavier hydrocarbons above C7.

Bibliography:

API Technical Data Book 1982 (Metric Edition) Ch 6 p. 39-42.

7.2.2 COSTALD

Available: PROCESS,PRO/II

Description: The corresponding states liquid density or COSTALD method is used for "LNG like" mixtures with excellent accuracy. The method uses two parameters to modify the individual pure component densities; one based on the acentric factor and one on experimental density data. It also corrects for high pressures using the Tait correlation.

Validity: Light hydrocarbons between C1-C8 only. No limits on pressure but the reduced temperature should be between 0.25 and 1.0.

Application: It is best suited for use with simple equations of state which cannot predict liquid densities on light hydrocarbon systems, i.e. NGL, LNG and LPG.

Key points: Developed with data for light C1-C5 hydrocarbons and should not be used outside this area. Also known as the Hankinson-Brobst-Thomson technique.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

7.2.3 Lee-Kesler

Available: PROCESS, PRO/II, PIPEPHASE

Description: Based on a corresponding states method.

Validity: Suitable for C1-C8 hydrocarbons only with reasonable accuracy but not applicable for heavier fluids. No limits on pressure but the reduced temperature should be between 0.25 and 1.0.

Application: As for COSTALD

Key points: C1-C8 hydrocarbons only. Inferior to COSTALD (7.2.2).

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

8. TRANSPORT PROPERTY METHODS

The prediction methods discussed in this section are rigorous methods based on pure component data. Simulation programs which run in non-compositional modes utilise correlations developed for oils or condensates based on bulk fluid properties. The exception to this is WIPCOG which is a compositional program but uses viscosity correlations. These correlations are far too numerous to be discussed here and the respective user guides contain all the relevant information for their use.

8.1 LIQUID AND VAPOUR VISCOSITY

Accurate prediction of liquid viscosity is extremely difficult to achieve due the number of variables involved; pressure, temperature, polarity and molecular profile. As a general statement, predicted viscosities are nearly always too low and this should be borne in mind when reviewing results.

Nearly all the methods rely on critical data developed from equations of state and so the choice of these directly affects the accuracy of the results. This is especially true for components above C20 where there is little or no experimental data available for critical properties.

If accurate viscosity data is required for design purposes it should be measured in a laboratory under the relevant conditions. KSLA has developed a program, LIVITHEC, for the prediction of viscosity and thermal conductivity for simple long chain molecules. It is not available for general use but if accurate data is required contact KSLA to assess its applicability before using the services of a laboratory.

8.1.1 Shell

Available: PRO/II(S), PROCESS(S), SHAMROCK, SMBP

Description: The program uses three methods of obtaining pure viscosity data: PEPPER, the TRAPP method for light components and the TWU method for heavy and pseudo components. For multi-component mixtures, a mixing rule based on volume fractions is used and a correction is applied to account for the effects of pressure.

Validity: The mixing rule produces significant errors if the mixture contains liquids with large viscosity ranges. Also, it is not suitable for high water content fluids as it cannot predict the formation of emulsions. If the pure component viscosity is not in PEPPER, the routine selects which method to use based on the temperature, pressure and molecular weight.

Application: Primarily for use with light hydrocarbons and water but not for heavy oils, polar fluids or chemicals. The action of chemicals on fluid viscosity must also be considered.

Key points: An understanding of the ranges for each correlation is essential.

Bibliography:

MFD 141/87 A. Langenberg. "Prediction of liquid viscosities".

ST/117/87 J. de Dood and C.L.M. Vrouwenvelder. "A comparative study of correlation models for the prediction of pure compound viscosity".

8.1.2 Commercial-PETRO

Available: PRO/II, PROCESS, PIPEPHASE

Description: The SimSci petro option selects one of four methods depending on the system temperature. The effect of pressure is accounted for using the modification in the API Data Book.

Validity: Reasonable results (within 10-30 percent) are obtained for alkanes but it is less accurate for use with polar, aromatic and napthenic compounds. Temperature and pressure ranges cover all normal EP applications.

Application: Alkane mixtures only and not for polar compounds. Suitable for heavy paraffinic hydrocarbons. For high water cut streams, only PIPEPHASE with the Woelflin mixing rule will give good results.

Key points: The use of SMIRK generated liquid densities does not improve the accuracy.

Bibliography:

API Technical Data Book 1982 (Metric Edition) Ch. 11 p47.

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

8.1.3 Commercial-TRAPP

Available: PROCESS, PIPEPHASE

Description: TRAPP (TRAnsport Properties Prediction) is a corresponding states type correlation which modifies the viscosity of a reference fluid by a factor related to the component's functional groups. It uses methane as its reference liquid and the factors are functions of reduced temperature, acentric factor and molar volume.

Validity: Not for use with water and only to C20 but ideally C1-C5. In PROCESS and PIPEPHASE it will only work for specific library components. When used on polar compounds, branched alkanes and napthalenes the errors increase towards 50 percent. Not for use with pseudo-components or petroleum fractions. Its main advantage is that it integrates the calculation method for both liquid and vapour viscosities and thermal conductivities.

Application: Ideal for LNG, NGL type fluids, i.e. simple alkanes with errors of 5-20 percent. It is valid for a wide range of temperatures and pressures. The use of SMIRK liquid densities helps prevent prediction of vapour viscosity close to saturation conditions but leads to an overall loss of accuracy. For high water cut streams, only PIPEPHASE with the Woelflin mixing rule will give good results.

Key points: Not recommended for general use on its own.

Bibliography:

"Properties of oils and natural gases". Pederson, Fredenslund and Thomassen. Gulf Publishing Company 1989.

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

8.1.4 Commercial-LOHRENZ

Available: PVTPACK, WIPCOG

Description: A fourth degree polynomial based on the reduced liquid density.

Validity: Suitable for most reservoir fluids except for very light condensates. It was developed using data from over 200 reservoirs over a wide composition range. Maximum temperature is 400 K.

Application: Developed specifically for use in reservoir simulators at reservoir conditions. Ideally for use with mixtures, it will predict trends rather than absolute values. An experimental calibration point is therefore required to determine a correction factor.

Key points: The accuracy of this method depends greatly on the accuracy of the liquid density measurement. Use at reservoir conditions only.

Bibliography:

Journal Petroleum Tech.1964 Vol 16 p. 1171 J.M. Lohrenz et al. "Calculating viscosities of reservoir fluids from their compositions".

EP 90-2325 A.R. van Bergen and K. van Leeuwen. "PVTPACK user guide". Appendix B.

8.2 SURFACE TENSION

8.2.1 Shell-PEWK

Available: PROCESS(S), PRO/II(S), WIPCOG, TWOPHASE, SHAMROCK, SMPB, VLEOS

Description: A KSLA modification of the Weinaug-Katz method which uses the concept of Parachors. Parachors are directly related to surface tension and can be considered as constants with respect to temperature. As surface tension depends on the properties of both the liquid and vapour phases, accurate densities are required for each. For mixtures, a molar average mixing rule is used and adjusted using binary data from PEPPER.

Validity: Valid for all EP applications. For pseudo-components, Parachors are calculated from the critical constants and the acentric factor. Hence, the accuracy of the result depends on the method used to develop the critical constants and to calculate liquid density (7.1 and 9.0).

Application: Suitable for all natural gas and condensate systems. Suitability with water and oil is good provided interaction data is available.

Key points: Can only be used with SMIRK and PEPPER. The results are very sensitive to changes in liquid density.

Bibliography:

AMGR 84.298 J.A. Hugill and A.J. van Welsens. "PEWK: A surface tension model for natural gas and condensate systems".

8.2.2 Commercial- API

Available: PROCESS, PRO/II, PIPEPHASE

Description: It is based on information from the API data book but with values for water being retrieved from the database. A correlation is used for hydrocarbon-water systems. This method is essentially the Weinaug-Katz technique used as the basis for PEWK (8.2.1)

Validity: Hydrocarbon and hydrocarbon-water systems only. For liquid mixtures containing methane the results are suspect unless very accurate liquid density data is available.

Application: For use in the SimSci PETRO transport properties option only.

Key points: It utilises a very simple mixing rule based on volume fractions.

Bibliography:

API Technical Data Book 1982 (Metric Edition) Ch. 10 p. 19.

8.3 LIQUID AND VAPOUR THERMAL CONDUCTIVITY

Thermal conductivity is also very difficult to predict for similar reasons as viscosity. If accurate thermal conductivity data is required it should be measured in a laboratory. The KSLA developed LIVITHEC program may provide an alternative option to laboratory measurement.

8.3.1 Shell

Available: PROCESS(S), PRO/II(S), SHAMROCK, SMBP

Description: Pure component data is available from PEPPER, the API data book or from the TRAPP (8.3.2) correlation. For mixtures, a volume based mixing rule is used which is corrected for pressure above 3500 kPa (API method).

Validity: Accuracy varies depending on the deviation of the molecules from basic unbranched hydrocarbons. Therefore, the heavier the compound the greater the possible error.

Application: Suitable for most EP applications unless actual data are available for cross checking.

Key points: Requires accurate density data.

Bibliography:

SIPM-MFD 141/87 A. Langenberg. "Prediction of liquid viscosities".

8.3.2 Commercial-TRAPP

Available: PROCESS, PIPEPHASE, PRO/II

The remarks for TRAPP are identical to PETRO (8.1.2).

8.3.3 Commercial-API

Available: PROCESS, PRO/II, PIPEPHASE

Description: Available in the PETRO option (8.1.2) and calculates liquid conductivities only. The mixing rule is based on weight averages with the API pressure correction applied at all pressures. Pure component values are retrieved from the database and two correlations are used with selection being dependent on the reduced temperature.

Validity: As for Shell method.

Application: All hydrocarbon - water systems.

Key points: Method selection depends on the system temperature. Accurate liquid density data is required.

Bibliography:

API Technical Data Book 1982 (Metric Edition) Ch. 12 p. 7-11.

9. PSEUDO-COMPONENT CHARACTERISATION

Arguably the most important aspect of basic data is the prediction of the heavy fraction physical properties. Small amounts of heavy components in a feed stream can significantly increase the rate of liquid dropout and possibly overload any separation or pumping system. This is because the mixture dew point is heavily dependent on the heaviest component in the mixture, therefore a small change in its K value has a marked impact on dew point. The old assumption that the heavy fraction can be modelled as a series of n-alkanes has been replaced by sophisticated analytical routines. As analytical technology progresses, PVT laboratories are reporting oil analyses to C20 thus improving the accuracy of the characterisation.

A selection tree for heavy ends characterisation and assignment of physical properties is given in (Appendix 6).

9.1 SPLITTING THE HEAVY FRACTION

Before any physical properties can be calculated, the heavy fraction must be split into a number of new or pseudo-components. The number of components selected has a significant impact on system behaviour especially for natural gas and gas condensate systems as the K value of the lumped fraction varies with the number of components used.

9.1.1 Shell-C7PLUS

Available: Stand alone, PRO/II(S), SHAMROCK, SMBP, PVTPACK

Description: Divides the heavy end fraction from a PVT report into discrete component fractions of given density and molecular weight whilst matching the overall or bulk values. The split may then be tuned using four variables to match measured field and laboratory data, i.e. saturation pressures and GOR's.

Validity: Suitable for use in EP applications for all types of reservoir fluids. For natural gas and gas condensate systems this routine mimics the sort of component distributions found in reality, i.e. non-exponential.

Application: The EP recommended routine for splitting the heavy fraction since it was developed to match measured component distributions in reservoir fluids. The output can be used in the FRACHAR physical property generator to assign pseudo-component critical and physical properties (9.2.1).

Key points: The program can generate a PROCESS input file but uses SRK and the API liquid density method as defaults. See (5.2.5 and 7.2.1). The program now forms an integral part of Shell PRO/II and it can be used to split the fraction, assign physical properties and check the saturation pressure all in a single step.

Bibliography:

EP 88-2515 J.N. Sutton A.Langenberg and J.D. Marshall. "A guide for heavy end characterisation of hydrocarbon stream".

Simsci PRO/II Input Manual. Shell Addendum, May 1991.

9.1.2 Shell-PVTPACK

Available: PVTPACK (subroutine only)

Description: The program splits the heavy fraction into aromatic and paraffinic pseudo-components and adjusts the ratio between them to match the bulk fraction molecular weight and a saturation pressure (optional). The output from this routine is then used by PETFR2 or GAMMA to assign component properties. See (9.2.2 and 9.2.3).

Validity: It assumes an exponential distribution of the heavy components and a constant paraffin to aromatic ratio. These assumptions are not always valid for light crudes and condensates.

Application: This method is used in PVTPACK only and the results from it can only be reliably used in PVTPACK, BOSIM or TEMPEST. This is because it utilises an equation of state to check the saturation pressure and so the same equation must be used in the main simulation.

Key points: As the routine generates a unique set of components using its own database the results should be used with caution in other phase behaviour programs.

Bibliography:

EP 53100. A.M. Schulte. "Representation of the C7+ fraction in phase equilibrium calculations".

EP 92-0665 W. Swinkles "Reservoir Engineering Guidlines for Gas Condensate Fields".

9.1.3 Commercial-SIMSCI

Available: PROCESS, PRO/II

Description: The SIMSCI method requires some form of assay curve before it can create pseudo-components. These curves can be simple True Boiling Point (TBP) curves with bulk MW or SG data or with MW and gravity curves. Once the component ranges have been specified several correlations can be used to calculate a specific gravity and MW for each pseudo-component (9.2.4 and 9.2.5).

Validity: The best form of heavy end data, excluding gas chromatograph analysis to C20, is an assay curve. There is no SimSci method capable of taking the MW and SG of the bulk heavy fraction and producing a set of pseudo-components which will match the bulk physical properties. If assay data are available, then the pseudo-components produced will be better than those produced by C7PLUS as the latter creates components to match the bulk data.

Application: Only for use when there is a TBP curve available with no MW or SG data for each range of boiling points.

Key points: The default correlations used to calculate MW and SG are not necessarily correct for the temperature ranges in the analysis.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

9.2 ASSIGNMENT OF PHYSICAL PROPERTIES

Once the pseudo-components have been created they must be assigned critical properties to allow them to be handled by an equation of state. In the case of SRK and SMIRK this means critical temperature and pressure, acentric factor, boiling point MW and density. The latter three will have been generated by the splitter routine but the first three are generated by specific physical property routines.

9.2.1 Shell-FRACHAR

Available: SHAMROCK, TWOPHASE, WIPCOG, PROCESS(S), PRO/II(S), SMBP

Description: Using individual fraction boiling point or molecular weight and liquid density, FRACHAR calculates the critical temperature and MW (if not specified), from correlations. It then guesses critical pressure and acentric factor to calculate a new boiling point and density using SMIRK. The cycle is then repeated until the figures match. Pseudo-components can be input from C7PLUS or defined separately.

Validity: Prediction of specific heat capacity is low (10-15 percent) especially for heavy aromatics. The alternative option, if it is important, is to use the correlations in STND

(5.1.1).

Application: All EP applications for all types of well fluid.

Key points: Care must be taken if FRACHAR is used to assign pseudo component properties and an equation of state other than SMIRK is specified in the simulation program. A check must then be made to ensure the phase behaviour with the new equation matches that in the PVT report.

Bibliography:

AMGR 84.123 J. de Dood and P. Heijink, "Characteristic constants of heavy hydrocarbons and petroleum fractions for physical property calculations: Development of FRACHAR".

RN/249/91 J. de Dood. "Calculation of specific heat capacities by FRACHAR".

9.2.2 Shell-PETFR2

Available: PVTPACK, HERCULES

Description: Determines the physical properties of the pseudo components generated from the PVTPACK heavy end splitting routine (9.1.2). It does not use an equation of state but two separate correlations: one for paraffins and one for aromatics. It is based on the principle of corresponding states and both correlations require boiling point data only.

Validity: Work by KSLA shows that the C7PLUS/FRACHAR combination gives consistently more accurate results than the PVTPACK/PETFR2 combination using the MRKS2 equation of state.

Application: For use in PVTPACK in combination with the C7+ splitting routine (9.1.2).

Key points: This routine is inferior to the GAMMA method (9.2.3) as the latter has the advantage that by varying gamma, more experimental data can be matched.

Bibliography:

EP 88-0708 L.N.J. de Jong and A.R.D van Bergen. "Characterisation of hydrocarbons by a corresponding states method."

EP 53100 (TPR-WRC 26.76) P.L. Chueh. "Characteristic constants of petroleum fractions for physical property calculations: Computer program PETFR2".

9.2.3 Shell GAMMA

Available: PVTPACK

Description: This routine calculates the component properties that are required by PVTPACK from the boiling point and aromaticity index, or gamma, of each fraction. The correlations used to achieve this were developed from a corresponding states approach. Values range from zero (alkanes) to 1 (highly aromatic). Gamma can be calculated from two other component properties.

Validity: This method was tested on all 68 components in the PVTPACK database (6.1.4) and proved accurate for nearly all hydrocarbons but not for non-hydrocarbons. The results from this method can be used with any other equation of state except SMIRK. The critical constants when used with SMIRK to describe liquid densities give errors of 10-20 percent.

Application: For use in combination with PVTPACK's heavy end splitting routine (9.1.2). Components generated by C7PLUS (9.1.1) can also be used as the routine will calculate gamma from molecular weight and specific gravity. This routine can also be used to calculate the properties of waxy components using melting point and molecular weight etc.

Key points: When used in conjunction with the splitting routine, values of gamma between 0.2 and 0.5 are recommended. The PETFR2 (9.2.2) correlation corresponds to a gamma of 0.35. In this method, members of the same homologous series do not have the same values of gamma.

Bibliography:

EP 88-0708 L.N.J. de Jong and A.R.D. van Bergen. "Characterisation of hydrocarbons by a corresponding states method".

9.2.4 Commercial- CAVETT et al.

Available: PROCESS, PRO/II, PIPEPHASE

Description: A series of correlations are used to generate critical properties, acentric factor, vapour pressure, etc. based on any 2 from 3 user supplied boiling point, specific gravity (SG) and MW data.

Validity: The correlations are valid for all temperatures seen in EP processes. They are best used for 'light' crudes.

Application: A useful method but inferior to FRACHAR (9.2.1). It should only be used when measured distillation data is available and not when only the MW and SG of the fraction are known.

Key points: If Cavett generated results are being used with an equation of state then bubble and dew points should be calculated to check the deviation from the known data.

Bibliography:

SimSci PROCESS Reference Manual, Rev. 2, December 1988.

API Technical Data Book 1982 (Metric edition) Ch2.

9.2.5 Commercial- TWU

Available: PROCESS, PRO/II, PIPEPHASE

Description: An extension of the method published in the API data book. Developed by SimSci.

Validity: Temperature range of 423-673 K. It is ideally suited for heavier type crudes with a SG greater 0.9.

Application: The same as (9.2.4)

Key points: The same as (9.2.4)

Bibliography:

API Technical Data Book 1982 (Metric Edition) Ch 2.

SIMSCI reference manuals.

10. NON-IDEAL PHASE BEHAVIOUR

For the majority of calculations, a simple treatment of hydrocarbon/water behaviour is sufficient. However, as the problems associated with waste minimisation and disposal increase, there is a greater demand to simulate the behaviour of such non-ideal systems. As a general statement, the basic data required for these simulations, primarily binary interaction data, is available in PEPPER although the quality is sometimes poor due to the quality of the experimental data used. This is currently being revised with an extensive research program aimed at obtaining new data for hydrocarbon-glycol/methanol systems. The SimSci database holds more binary data for the SRKM equation of state but of unknown quality albeit from quality databases (Appendices 4 and 5).

10.1 LIQUID-LIQUID SYSTEMS

10.1.1 Hydrocarbon/water

This can be broken down into two areas: the solubility of oil in water and vice versa. Until recently, process engineers were only interested in the latter as it directly affected the final product specification. However due to the high cost of processing dirty water, accurate predictions of oil in water are now essential.

All phase behaviour methods assume an equilibrium is reached. This is an idealised situation as in reality emulsions may form due to high shear rates across control valves. In addition, corrosion inhibitors will seriously affect oil/water equilibria by holding water in the oil phase.

10.1.1.1 Water In Oil

There are correlations available for use with SRK, PR and GS equations. The amount of water dissolved in oil is calculated either using correlations developed for kerosene or based on the water solubility in individual components. Solubilities in pseudo-components are calculated via correlations. The remaining water is then decanted off as a pure water stream. An alternative method is to use SMIRK or SRKKD and utilise the interaction coefficients to calculate solubility.

For streams which have high water cuts, the normal mixing rules are invalid as they do not account for the formation of emulsions. The best method is to use the Woelflin mixing rule as found in PIPEPHASE.

10.1.1.2 Oil In Water

Some correlations do exist but rigorous three phase calculations are required to give accurate results. Both SMIRK or SRKKD will give similar results but these equations rely on the use of binary data and the accuracy of the results can only be as good as the amount and accuracy of the data available. See (Appendices 3 and 5). If data is not available, then a fill-in method such as UNIFAC will provide a better estimate than an assumption of ideality. It should also be remembered that all the SMIRK interaction coefficients and generalisations were developed from limited data for the water rich phase. The published data in this area is limited and conflicting. However, this will improve in the future.

If binary data are not available for all the important binaries and the system is at a low pressure, the NRTL methods will give more accurate results provided all the parameters for this method are available.

These types of calculations use up a great deal of CPU time and should only be specified where necessary. For example, on a crude stripper three phases will only exist on the top one or two stages, therefore VLLE calculations need only be specified for those stages.

A recent development in EP operations is the use of air or steam to strip both dissolved and dispersed hydrocarbons from water. Recent work in SIPM shows that the best way to model such systems is to use Henry's coefficients obtained through pilot plant trials or from the Environmental Protection Agency database.

10.1.2 Aromatics/water

If the system contains aromatics only, then any simple equation of state will suffice, e.g. SRK. If water is present, NRTL should be considered provided the pressure is low. At higher pressures, SMIRK or SRKM are the better options. For uncommon aromatic compounds, the generalisations used to calculate interaction coefficients may not be accurate.

Use API or COSTALD with SRKM to calculate liquid densities.

10.1.3 Methanol/water

Depending on the data available, NRTL will yield the best results for liquid-liquid systems. However, the pressures generally need to be below 1000 kPa and interaction coefficients are required for all components. If using PROCESS or PRO/II then any missing data should be filled in with UNIFAC. The results should be analysed very carefully to pick up rogue results.

SRKM gives excellent results with methanol but SMIRK is considered to be less accurate for the calculation of methanol solubility in hydrocarbons and water as there are only correlations and no specific binary data available. Ideal methods should not be used under any circumstances, e.g. STND treats methanol as a hydrocarbon.

Operational data is urgently required to allow comparisons to be made between different methods. At present only laboratory data is available.

10.1.4 Hydrocarbon/Glycol

For this to be simulated accurately, binary data are required for hydrocarbons and glycol. Within PRO/II, the SRKM equation has a limited set of interaction coefficients for MEG, DEG and TEG fitted over the normal range of temperature and pressures encountered within EP. In version 3.02, some of these have to be input manually due to a program bug. This has been corrected in version 3.1. The PEPPER database does have some coefficients for TEG but those for MEG and DEG have been regressed from very limited data (C1-C3) and are not recommended for use unless the results are for estimations only. When considering aromatic/glycol binaries, the KSLA data are even more limited some of which are not yet available in PEPPER. See (Appendix 5). In general there is a lack of useful experimental data for glycol systems.

Bibliography:

EP 88-0098. J. de Dood et al. "Glycol basic data. Measurement and correlation of mutual solubilities in glycol hydrocarbon systems".

10.2 SOUR GASES

When the concentration of sour gases or inerts is above five percent then the correlations used to calculate interaction parameters are less accurate. The problem with carbon dioxide is that, under normal EP conditions, this component is close to its critical point. If the equation of state is not tailored to match near this point then the results will be erroneous. The problem any equation of state has is that they cannot determine the phase especially when one liquid phase is already present.

The best option is to remain with SMIRK but supply new interaction parameters after consultation with KSLA. There is limited binary data available for light hydrocarbons with carbon dioxide and hydrogen sulphide and PEPPER contains generalisations for both carbon dioxide and hydrogen sulphide with hydrocarbons. See (Appendix 5).

10.3 TRACE METALS

The distribution of heavy metals between phases is becoming very important especially where mercury is involved.

Mercury removal systems are becoming more common and the ability to predict mercury levels is essential to ensure correct equipment sizing, operational life and environmental control (i.e. collection and acceptable disposal/recycle of the mercury).

11. SYSTEM RECOMMENDATIONS

The comments below refer to compositional simulations only. When running non-compositionally, the selection of correlations is fixed by the nature of the fluid and the physical conditions.

In PRO/II there is an 'expert' thermodynamics selection system to advise the user on thermodynamic system selection. This appears to be useful but it should not be considered infallible. It cannot replace a series of rational decisions based on understanding the nature of the simulation to be performed and knowledge of the various options available. A simple thermodynamic method selection tree is given in (Appendix 8).

11.1 NATURAL GAS

For natural gas systems with less than five mol percent inerts, any general equation of state will give excellent results. This is because they were all developed using data for light hydrocarbons. Close to the critical point, all equations will suffer from inaccuracy, especially SMIRK, therefore operation close to this point should be avoided. If there are high levels of inerts, then SRKM or SMIRK are ideally suited as they allow the use of extensive interaction data.

It is important that the heavy component 'tail' is characterised accurately as this dictates the shape of the phase envelope dew point line and therefore the predicted cricondentherm. Use C7PLUS within PRO/II(S) to create the pseudo-components and either FRACHAR or CAVETT to generate their physical properties. Using PRO/II(S) eliminates the need to transfer files between applications and reduces the time required to complete a characterisation. The choice of which method to use depends on which equation of state is selected for use in the main program. FRACHAR uses SMIRK to calculate the critical pressure and acentric factor so care should be exercised if SMIRK is not being used in the main simulation as the predicted phase envelope may have altered significantly.

If the SMIRK equation of state is not specified, then the COSTALD liquid density method should be used both in the main simulation and during the characterisation process. Users of PVTPACK can only utilise the BWRS density method which gives relatively poor results.

The choice of interaction parameter sets is governed by the equation of state. A check should be made to ensure that binary data is available for the most important binaries.

For the majority of applications the 'kerosene' correlations for water solubility in oil will be adequate. However, if more accurate data are required, either SMIRK or SRKKD should be used. For oil in water data, then either SMIRK, SRKKD or NRTL are recommended (provided the pressure is below 1000 kPa). If the results are to be used as design data the only reliable method is to recreate the process conditions in a laboratory. This has been successfully achieved by KSLA in the past.

Where other non-polar components are present, such as methanol, then either SMIRK or SRKM is recommended. As discussed above, the results should be used with care and if critical should be measured in a laboratory.

Transport options with Shell methods are fixed in PRO401S but not in PRO/IIS where the SimSci methods are available. However, with the SIMSCI methods, it is best to use the Library option and with PVTPACK-SRK only the Lohrenz method is available for viscosity prediction.

11.2 GAS CONDENSATE

Use SRK, PR or SMIRK for the majority of applications with an appropriate method for liquid density, e.g. SMIRK or COSTALD.

Use C7PLUS for the creation of the pseudo components and either FRACHAR or CAVETT to generate their physical properties. As with Natural Gas systems it is most important that the heavy end is accurately characterised.

If water solubility in the condensate phase is a concern, then use either SMIRK in VLLE mode or SRKKD. Only use SRKKD when necessary as it uses more CPU time, e.g. on top of water strippers where three phases exist in equilibrium. For the solubility of condensate in water then it is a direct choice between SMIRK, SRKM and NRTL, provided the pressures are low. NRTL is especially good if there are significant quantities of aromatics. The availability of binary data must be checked by including the keyword INPUT = ALL under PRINT option in PRO/II to avoid erroneous results. The lack of binary data can be filled in using UNIFAC with the SimSci NRTL method. This option is not available with the Shell NRTL method.

Where other polar components are present, such as methanol or glycol, then either SMIRK or SRKM is recommended. Binary data for glycol, especially MEG and DEG, is limited and of unknown quality.

Transport options with Shell methods are fixed in PRO401S but not in PRO/IIS where the SimSci methods are available. However, with SIMSCI it is best to use the PETRO option and with PVTPACK-SRK only the Lohrenz method is available for viscosity prediction.

11.3 BLACK OIL

Use SRK, PR or SMIRK for the majority of applications with an appropriate method for liquid density, e.g. SMIRK or API.

Use C7PLUS for the creation of the pseudo components and either FRACHAR or TWU to generate their physical properties. Unlike natural gas and gas condensate systems, detailed characterisation of the heavy fraction is not essential. This is because the fraction is so large, up to 60-70 percent, that the overall phase behaviour is dominated by the light components.

For hydrocarbon solubility in water use of the kerosene option with SRK or PR will suffice. For the vapour phase the GPSA option is probably the most accurate especially at high pressures. SMIRK in VLE mode will yield similar results.

Where the solubility of hydrocarbon in water is significant then use either SMIRK or SRKKD provided there is no methanol present. The accuracy of the results will depend on the correlations used to generate binary data for the pseudo-components. All output should be analysed carefully for rogue results.

The viscosity prediction methods used in the Shell methods, PROCESS and PRO/II are inaccurate for high water content streams.

APPENDICES

Appendix 1	Generalised expressions for SMIRK binary interaction coefficients
Appendix 2	Generalised expressions for SMIRK binary interaction coefficients with water
Appendix 3	Presence of binary interaction coefficients for SRKKD method in SIMSCI database
Appendix 4	Presence of binary interaction coefficients for SRKM method in SIMSCI database
Appendix 5	Presence of binary interaction coefficients (SMIRK) and experimental data
Appendix 6	Selection tree for heavy ends characterisation
Appendix 7	Availability matrix of phase behaviour models and simulation programs
Appendix 8	Thermodynamic methods selection tree

APPENDIX 1 GENERALISED EXPRESSIONS FOR SMIRK BINARY INTERACTION COEFFICIENTS

SMIRK binary interaction coefficients K_{ij}, where j = hydrocarbon

Hydrogen $K_{ij}^{o} = 0.4731 - (0.0464\ \mathrm{UOPK}) + 0.5704T_r$

Carbon dioxide $K_{ij}^{o} = 0.0847 + 0.0502/T_c$

Carbon monoxide $K_{ij}^{o} = 0.4604 - 0.2581\omega$

Nitrogen $K_{ij}^{o} = 0.094$

Methanol $K_{ij}^{o} = 0.06V_c - 0.016$

$K_{ij}' = -0.215 - 0.08V_c + 5E\text{-}4\ T$

Hydrogen Sulphide $K_{ij}^{o} = 0.142\ T_c - 0.059$

Ethylene glycol $K_{ij}^{o} =$ 0.3105 for paraffins

= 0.8 38 for n-alkyl benzenes

= 0.3240 for n-alkyl naphtenes

= 0.273 for other hydrocarbons, pseudo-component

Diethylene glycol $K_{ij}^{o} =$ 0.05 (Rough approximation)

Where,

UOPK = Watson coefficient for the hydrocarbon

T_r = Reduced temperature of the hydrocarbon

T_c = Critical temperature of the hydrocarbon (K)

T = Temperature of the hydrocarbon (K)

V_c = Critical volume of the hydrocarbon (m^3)

ω = Acentric factor for the hydrocarbon

APPENDIX 2 GENERALISED EXPRESSIONS FOR SMIRK BINARY INTERACTION COEFFICIENTS WITH WATER

SMIRK binary interaction coefficients K_{ij}, where i = water and j = hydrocarbon

General expression for $K_{ij}^{\circ} = \theta^{o} + \theta^{o}_{t}T$

$K_{ij}' = \theta' + \theta'_{t}T$

For alkanes and aliphatic compounds (PEPPER compounds. Type D, O, P, T, W)

θ^{o} = -0.00136 MW

θ^{o}_{t} = 0.0001845 + 2.5E-6 MW

θ' = 0.00139 MW - 0.6706

θ'_{t} = 6.626E-4 - 2.4E-6 MW

For alkylnaphthenes (PEPPER groups C, J, M, N, V)

θ^{o} = -0.255 - 2.79E-4 MW

θ^{o}_{t} = 0.00105 - 8.34E-7 MW

θ' = -0.3904 - 0.000443 MW

θ'_{t} = 2.07E-6 MW

For alkylaromatics and alkylnaphthalenes (PEPPER groups A, B, F, G, H, I, S)

θ^{o} = -2.956 + 0.317 UOPK - 0.00584 MW

θ^{o}_{t} = 0.00912 + 9.39E-4 UOPK +1.46E-5 MW

θ' = -1.1356 + 0.1272 UOPK - 0.00333 MW

θ'_{t} = 0.00476 - 6.13E-4 UOPK + 1.8E-5 MW

For pseudo component petroleum fractions

θ^{o} = -0.7857 + 0.0533 UOPK- 3.91E-4 MW

θ^{o}_{t} = 0.00279 - 1.82E-4 UOPK

θ' = 1.0686 - 0.127 UOPK + 2.81E-4 MW

θ'_{t} = -0.00278 - 2.49E-4 UOPK

Where,

UOPK = Watson coefficient for the hydrocarbon
T = Temperature (K)
MW = Molecular weight of the hydrocarbon

APPENDIX 3 PRESENCE OF BINARY INTERACTION COEFFICIENTS FOR THE SRKKD METHOD IN SIMSCI DATABASE

	CO_2	N_2	H_2S	H_2O	MEG	DEG	TEG	MeOH	1P	2P	3P	4P	5P	6P	7P	8P	9P	10P	6A	7A	8A
CO_2																					
N_2	░																				
H_2S	░	░																			
H_2O	░	░	░																		
MEG	▨	▨	▨	▓																	
DEG	▨	▨	▨	▓	▓																
TEG	▨	░	░	▓	▓	▓															
MeOH	░	░	░	░	▓	▓	▓														
1P	░	░	░	☒	▓	▓	▓	░													
2P	░	░	░	☒	▓	▓	▓	░	░												
3P	░	░	░	☒	▓	▓	▓	░	░	░											
4P	░	░	░	☒	▓	▓	▓	░	░	░	░										
5P	░	░	░	☒	▓	▓	▓	░	░	░	░	░									
6P	░	░	░	☒	▓	▓	▓	░	░	░	░	░	▓								
7P	░	░	░	☒	▓	▓	░	░	░	░	░	░	░	░							
8P	░	░	░	☒	▓	▓	░	░	░	░	░	▓	░	▓	▓						
9P	░	▨	░	☒	▓	▓	▓	▓	░	░	░	▓	▓	▓	▓	▓					
10P	░	░	░	☒	▓	▓	░	░	░	░	░	░	▓	▓	▓	▓	▓				
6A	░	░	▨	☒	▓	░	▓	░	░	░	░	▓	░	░	░	░	▓	▓			
7A	░	▨	▨	☒	▓	░	░	▓	░	░	░	▓	▓	▓	▓	▓	▓	▓	▓		
8A	▨	▨	▨	☒	▓	▓	░	▓	░	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	

☒ KD binaries

░ SRK binaries

▓ No binaries available

▨ Correlations

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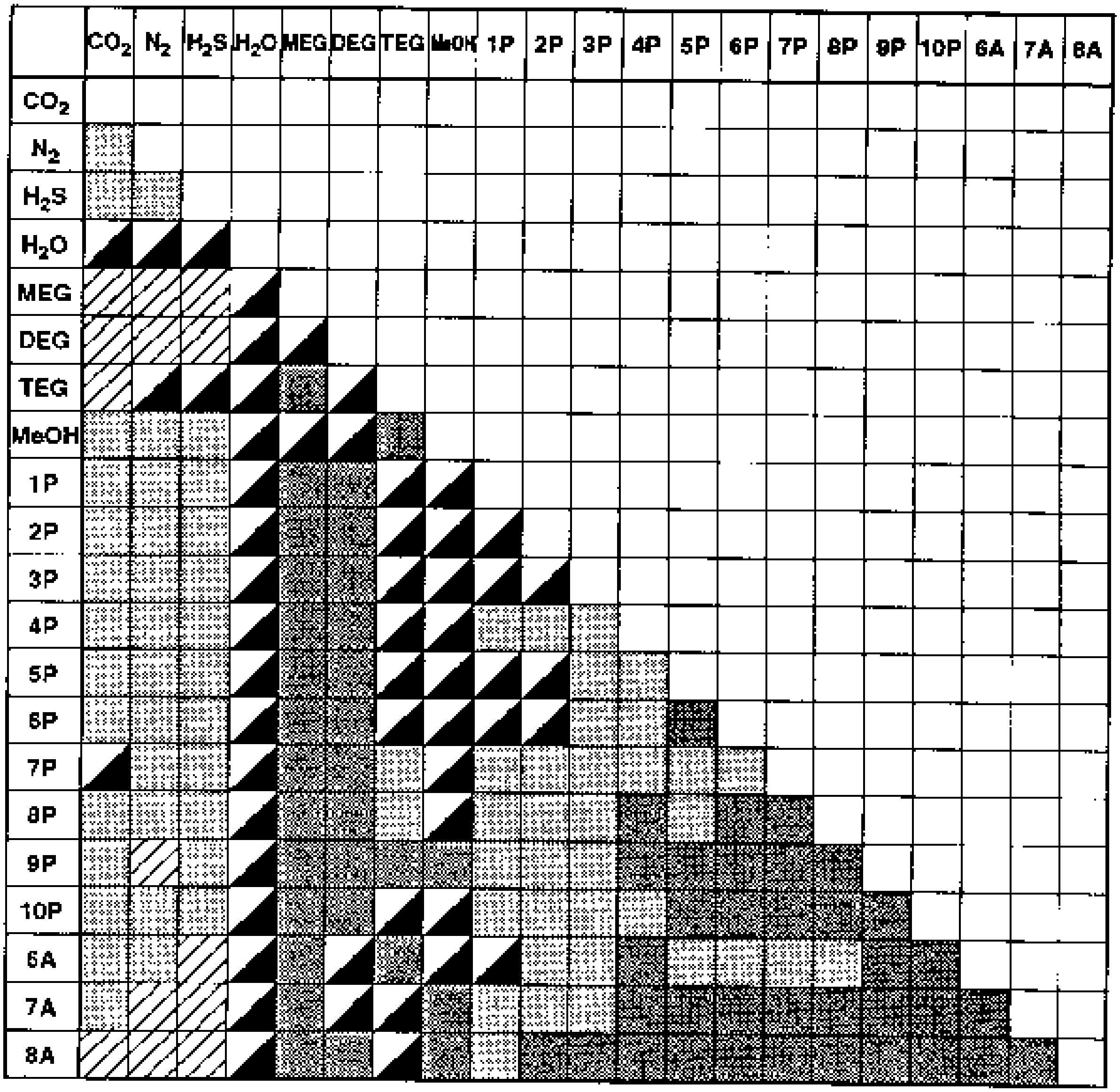
APPENDIX 4 PRESENCE OF BINARY INTERACTION COEFFICIENTS FOR THE SRKM METHOD IN SIMSCI DATABASE



	CO_2	N_2	H_2S	H_2O	MEG	DEG	TEG	MeOH	1P	2P	3P	4P	5P	6P	7P	8P	9P	10P	6A	7A	8A
CO_2																					
N_2	░																				
H_2S	░	░																			
H_2O	◪	◪	◪																		
MEG	▨	▨	▨	◪																	
DEG	▨	▨	▨	◪	◪																
TEG	▨	◪	◪	◪	▓	◪															
MeOH	░	░	░	◪	◪	◪	▓														
1P	░	░	░	◪	▓	▓	◪	◪													
2P	░	░	░	◪	▓	▓	◪	◪	◪												
3P	░	░	░	◪	▓	▓	◪	◪	◪	◪											
4P	░	░	░	◪	▓	▓	◪	◪	░	░	░										
5P	░	░	░	◪	▓	▓	◪	◪	◪	◪	░	░									
6P	░	░	░	◪	▓	▓	◪	◪	◪	◪	░	░	▓								
7P	◪	░	░	◪	▓	▓	░	◪	░	░	░	░	░	░							
8P	░	░	░	◪	▓	▓	░	◪	░	░	░	▓	░	▓	▓						
9P	░	▨	░	◪	▓	▓	▓	▓	░	░	░	▓	▓	▓	▓	▓					
10P	░	░	░	◪	▓	▓	◪	◪	░	░	░	░	▓	▓	▓	▓	▓				
6A	░	░	▨	◪	▓	◪	▓	◪	◪	░	░	▓	░	░	░	░	▓	▓			
7A	░	▨	▨	◪	▓	◪	◪	▓	░	░	░	▓	▓	▓	▓	▓	▓	▓	▓		
8A	▨	▨	▨	◪	▓	▓	◪	▓	░	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	

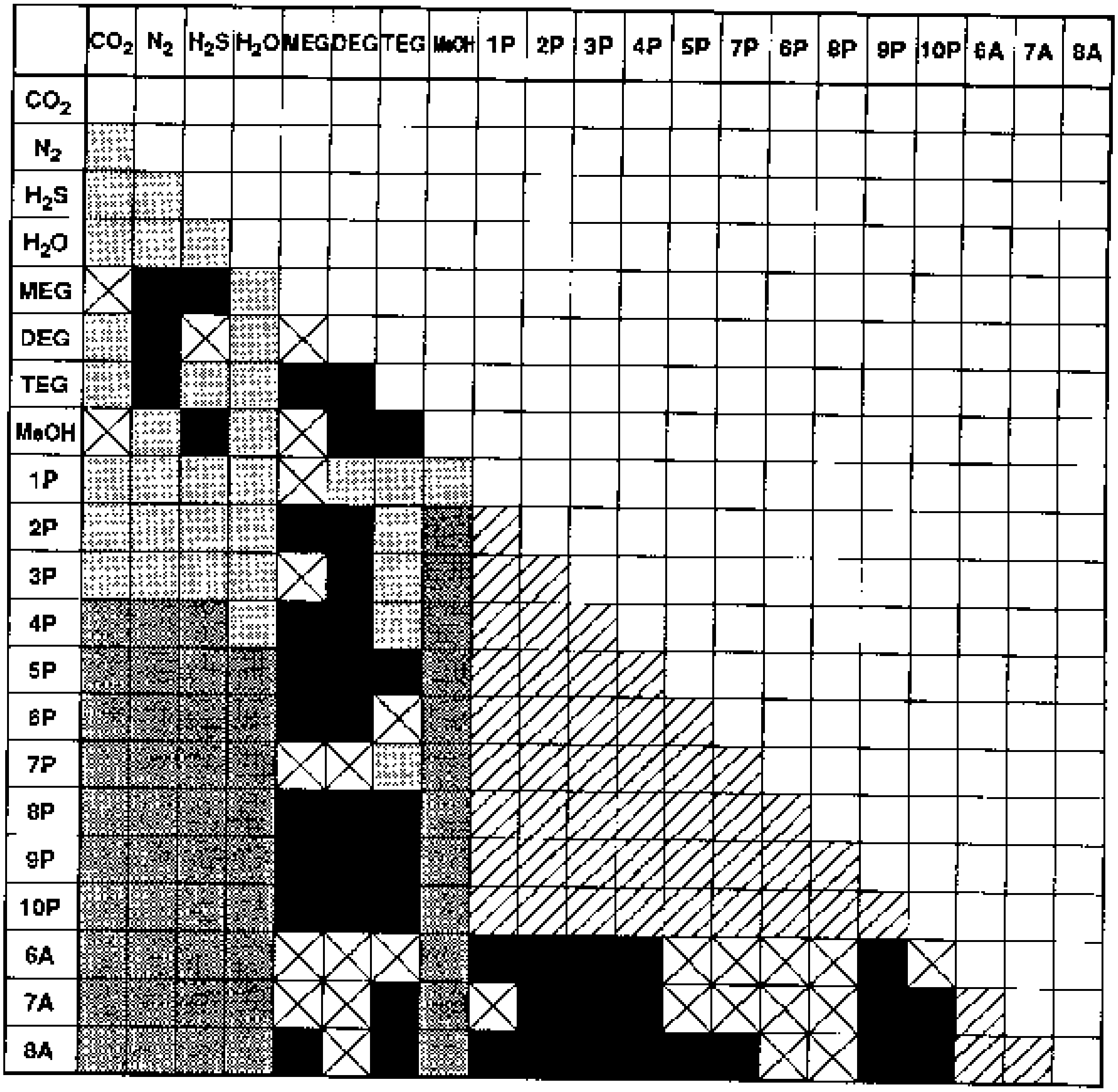
◪ SRKM binaries

░ SRK binaries

▓ No binaries available

▨ Correlations

APPENDIX 5 PRESENCE OF BINARY INTERACTION COEFFICIENTS (SMIRK) AND EXPERIMENTAL DATA



	CO_2	N_2	H_2S	H_2O	MEG	DEG	TEG	MeOH	1P	2P	3P	4P	5P	7P	6P	8P	9P	10P	6A	7A	8A
CO_2																					
N_2	░																				
H_2S	░	░																			
H_2O	░	░	░																		
MEG	☒	■	■	░																	
DEG	░	■	☒	░	☒																
TEG	░	■	░	░	■	■															
MeOH	☒	░	■	░	☒	■	■														
1P	░	░	░	░	☒	░	░	░													
2P	░	░	░	░	■	■	░	▒	▨												
3P	░	░	░	░	☒	■	░	▒	▨	▨											
4P	▒	▒	▒	░	■	■	░	▒	▨	▨	▨										
5P	▒	▒	▒	▒	■	■	■	▒	▨	▨	▨	▨									
6P	▒	▒	▒	▒	■	■	☒	▒	▨	▨	▨	▨	▨								
7P	▒	▒	▒	▒	☒	☒	░	▒	▨	▨	▨	▨	▨	▨							
8P	▒	▒	▒	▒	■	■	■	▒	▨	▨	▨	▨	▨	▨	▨						
9P	▒	▒	▒	▒	■	■	■	▒	▨	▨	▨	▨	▨	▨	▨	▨					
10P	▒	▒	▒	▒	■	■	■	▒	▨	▨	▨	▨	▨	▨	▨	▨	▨				
6A	▒	▒	▒	▒	☒	☒	☒	▒	■	■	■	■	☒	☒	☒	☒	■	☒			
7A	▒	▒	▒	▒	☒	☒	■	▒	☒	■	■	■	☒	☒	☒	☒	■	■	▨		
8A	▒	▒	▒	▒	■	☒	■	▒	■	■	■	■	■	■	☒	☒	■	■	▨	▨	

░ Binary interaction coefficients present in PEPPER

▒ Generalisation

▨ Binaries for which optimisation is not (yet) necessary

☒ Experimental data present in KSLA data banks

■ No data available

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APPENDIX 6 SELECTION TREE FOR HEAVY ENDS CHARACTERISATION

APPENDIX 7 AVAILABILITY MATRIX OF PHASE BEHAVIOUR MODELS AND SIMULATION PROGRAMS

PROGRAM	**PHASE BEHAVIOUR MODELS**														
	STND	BRAUN K10	GS	SMIRK	MRKS1	MRKS2	BWRS	SRK	SRKKD	SRKM	PR	SNRTL	NRTL	UNIFAC	HEN LA
SMBP	**X**			**X**								**X**			
VLEOS				**X**								**X**			
PVTPACK				**X**	**X**	**X**	**X****				**X**				
SHAMROCK	**X**			**X**								**X**			
WIPCOG				**X**											
TWOPHASE				**X**											
PIPEPHASE		**X**	**X**					**X**			**X**				
PROCESS	**X**	**X**	**X**	**X**			**X**	**X**	**X**		**X**	**X**	**X**	**X**	**X**
PRO/II	**X**	**X**	**X**	**X**			**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
HERCULES						**X**					**X**				
ASPEN+				**X**				**X**				**X**			
FRACHAR*				**X**											

* subroutine only
** for liquid density only

APPENDIX 8 THERMODYNAMIC METHODS SELECTION TREE