Chapter III

Equations of State

Equipment design procedures for separation operations phase enthalpies and densities in addition to phase equilibrium ratios. Classical thermodynamics provides a means for obtaining all these quantities in a consistent manner from P-v-T equations have been proposed, relatively few are suitable for practical design calculations.

All equations of state can be applied to mixtures by means of *mixing rules* for combining pure species constants. The ideal gas equation is widely applied to pure gases and gas mixtures. This equation neglects molecular size and potential energy of molecular interactions. When each species in a mixture, as well as the mixture, obeys the ideal gas law, both Dalton's law of additive partial pressures and Amagat's law of additive pure species volumes apply. The mixture equation in terms of molal density ρ/M is

$$\rho/M = 1/v = P/RT = (\sum_{i=1}^{c} n_i)/V \qquad (3.1)$$

The ideal gas law is generally accurate for pressures up to one atmosphere. At 50 Psia(344.74 KPa),(3.1)can exhibit deviations from experimental data as large as 10%.

No corresponding simple equation of state exists for

vopor and liquid phases.Although the Benedict-Webb-Rubin(B-W-R)equation of state has received the most attention,numerous attempts have been made to improve the much simpler R-K equation of state so that it will predict liquid-phase properties with an accuracy comparable for the vapor phase. The major difficulty with the original R-K equation is its failure to predict vapor pressure accurately,as was exhibited
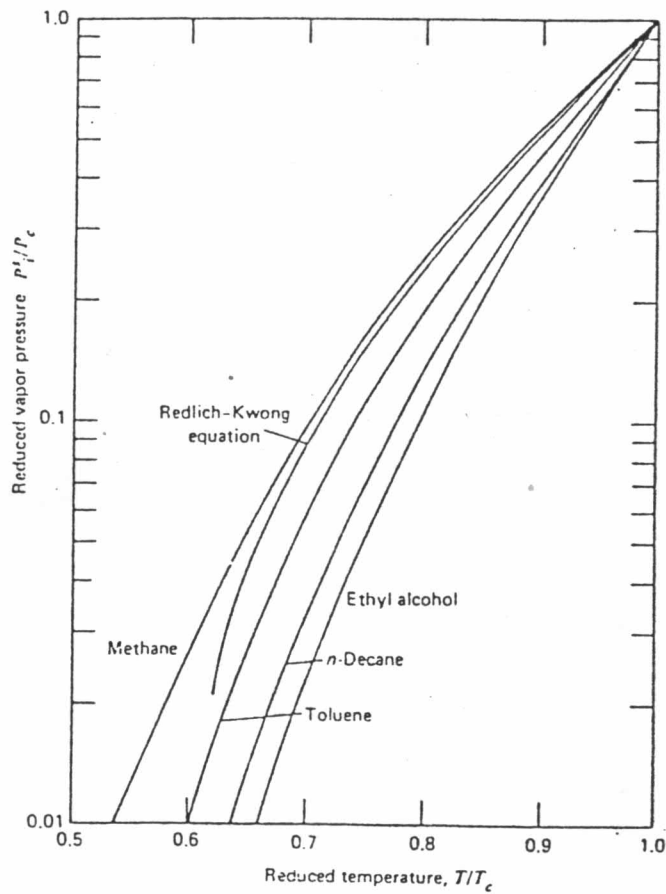

Figure 3.1 Reduced vapor pressure.

From Ernest,J.H. and Seader,J.D.

in Fig.3.1 Soave added a third parameter,the Pitzer acentric factor,to the R-K equation and obtained almost exact agreement with pure hydrocarbon vapor pressure data.The S-R-K equations appear to give the most reliable overall results for K-values and enthalpies over wide ranges of temperature and pressure.However the S-R-K correlation,like R-K equation, still fails to predict liquid density with good accuracy.A more recent extension of the R-K equation by Peng and
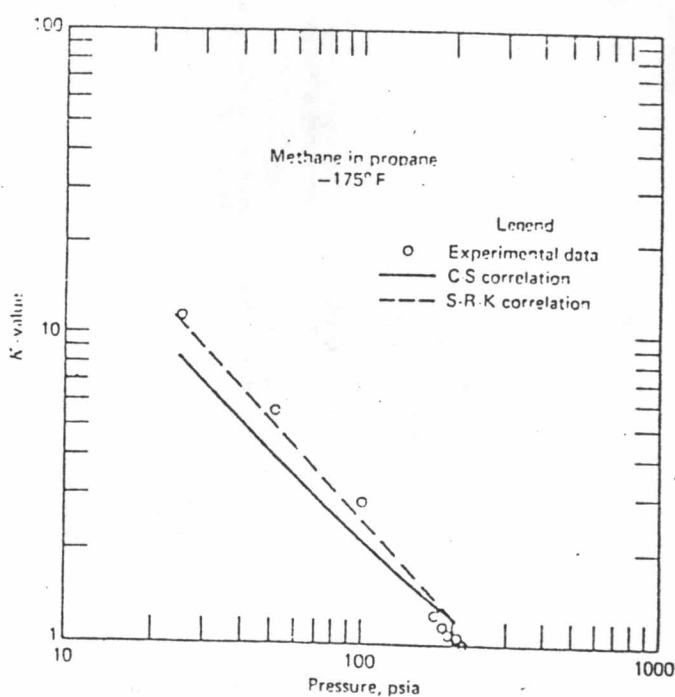

Figure 3.2 K-value for methane in propane at cryogenic conditions. (Data from R. H. Cavett, "Monsanto Physical Data System," paper presented at AIChE meeting, 1972, and E. W. West and J. H. Erbar, "An Evaluation of Four Methods of Predicting Thermodynamic, Properties of Light Hydrocarbon Systems," paper presented at NGPA meeting, 1973.)

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Robinson is more successful in that respect. The S-R-K correlation appears to be particularly well suited for predicting K values and enthalpies for natural gas systems at cryogenic temperatures,where the C-S correlation is not always adequate.Figure 3.2 and 3.3 which are based on the data of Cavett and West and Erbar are comparisons of K-values computed for the C-S and S-R-K correlations to experimental K-values of Wichterle and Kobayashi for methane-propane system
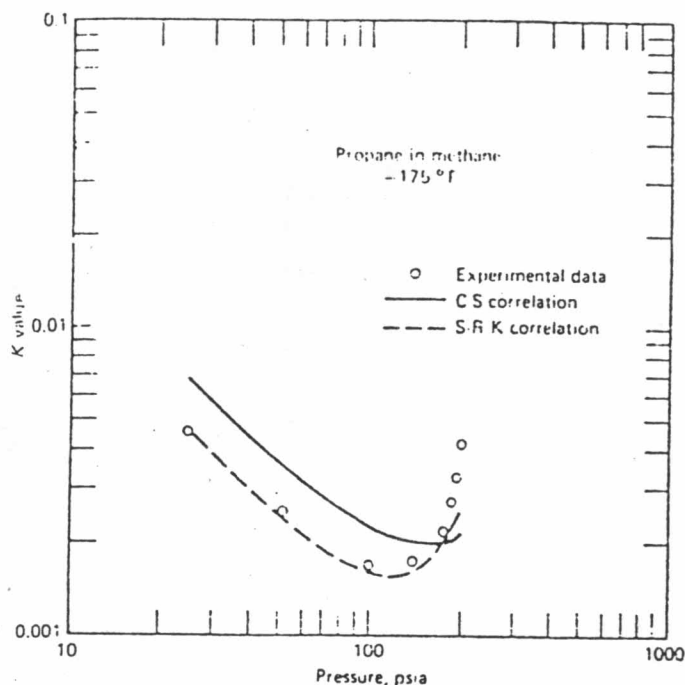

Figure 3.3 K-value for propane in methane at cryogenic conditions. (Data from R. H. Cavett, "Monsanto Physical Data System," paper presented at AIChE meeting, 1972, and E. W. West and J. H. Erbar, "An Evaluation of Four Methods of Predicting Thermodynamic Properties of Light Hydrocarbon Systems," paper presented at NGPA meeting, 1973.)

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the liquid phase other than one based on the use of a known pure species liquid density and the assumptions of incompressibility and aditive volumes. When a vopor is not an ideal gas,formulation of an accurate equation of state becomes difficult because of the necessity to account for molecular interactions.

Soave-Redlich-Kwong Equation of State

The Soave modification of the Redlich-Kwong equation of state is shown to work well Graboski and Daubert(1978) for the estimation of the vapor-liquid equilibrium behavior of a wide variety of technically important hydrocarbon mixtures. The American Petroleum Institute's Technical Data Book, Petroleum Refining recently adopted a modified Soave procedure for vapor-liquid equilibria calculations.The complete correlation is fully generalized,requiring only the readily available characterization parameters to make equilibrium calculations.

Soave(1972)originally proposed a modification of the Redlich-Kwong equation of state which introduced a third parameter,the acentric factor,and a temperature dependency into the cohesive energy term to account for the effect of nonsphericity on fluid P-V-T properties. Thermodynamic properties of nonideal hydrocarbon mixtures can be predicted by a single equation of state if it is valid for both the

at -175 $F^{\circ}(-115$ $C^{\circ})$over the pressure range of 25 to approximately 200 psia(0.172 to 1.379 MPa).While the S-R-K correlation follows the experimental data quite closely,the C-S correlation shows average deviations of approximately 16% and 32% for methane and propane,respectively.The Soave-Redlich-kwong equation is rapidly gaining acceptance by the hydrocarbon processing industry.Further developments,such as that of Peng-Robinson,are likely to improve predictions of liquid density and phase equilibria in the critical region.In general however,used of such equations appears to limited to relatively small,nonpolar molecules.Calculations of phase equilibria with S-R-K equations require initial estimates of the phase compositions.The Soave modification of the Redlich-Kwong equation of state has the following form:

$$P = RT/(v-b)-a/(v(v+b)) \qquad (3.2)$$

Where a and b in a mixture are found from

$$b = \sum_i \sum_j y_i y_j b_{ij} \qquad (3.3)$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \qquad (3.4)$$

$$a_{ii} = \alpha(T)(0.42748R^2 T_{ci}^2/p_{ci}) \qquad (3.5)$$

where $\alpha_i(T) = [1+m_i(1-\sqrt{T/T_{ci}})]^2 \qquad (3.6)$

$$m_1 = 0.480+1.574w_1-0.176w_1^2 \qquad (3.7)$$

and
$$b_{11} = 0.08664RT_{c1}/p_{c1} \qquad (3.8)$$

$$a_{1j} = (1-k_{1j})\sqrt{a_{11}}\sqrt{a_{jj}} \qquad (3.9)$$

$$b_{1j} = (b_{11}+b_{jj})/2 \qquad (3.10)$$

$$A = aP/R^2T^2 \qquad (3.11)$$

$$B = bP/RT \qquad (3.12)$$

$$Z^3-Z^2+Z(A-B-B^2)-AB \qquad (3.13)$$

Z :compressibility of mixture

k_{1j} :binary interaction parameters

for pure components:

$$Z^3-Z^2+Z(A_1-B_1-B_1^2)-A_1B_1 \qquad (3.14)$$

$$A_1 = a_{11}P/R^2T^2$$

$$B_1 = b_{11}P/RT$$

$$V = ZRT/P$$

In(3.14) Z is the compressibility factor for the pure species.

$$\ln\phi_1^\circ = Z-1-\ln(Z-B_1)-A_1/B_1\ln((Z+B_1)/Z) \qquad (3.15)$$

$$\ln f_1^\circ = \ln P+\ln\phi_1^\circ$$

$$\ln(\phi_1) = (Z-1)B_1/B-\ln(Z-B)-(A/B)[2(A_1^{0.5}/A^{0.5})$$

$$-B_1/B]\ln((Z+B)/Z) \qquad (3.16)$$

$$\ln f_1 = \ln P+\ln\phi_1$$

The resulting expressions are applicable to either the liquid or vapor phases provided that the appropriate phase

composition and compressibility factor are used. Equation (3.15),(3.16)can be used to calculate fugacity coefficients of pure species and mixture in both liquid and vapor phases at equilibrium. In these calculations,the compressibility factor Z for pure species and mixture are obtained by solving equation (3.14),(3.13) respectively. The largest root of equation (3.14),(3.13)are used to evaluate gas-phase fugacity coefficients; the smallest root of equation (3.14),(3.13)are used to evaluate liquid-phase fugacity coefficients. Newton-Raphson calculational technique with initial estimates of the compressibility factor being set at 1 for the gas phase and 0 for the liquid phase.

In general case, the hydrocarbon mixture system two-constant equation of state can be considerably reduced if all the binary interaction parameters(k_{ij} values) are equated to zero.The S-R-K equations can also be applied to light gases such as nitrogen ,carbon dioxide,carbon monoxide and hydrogen sulfide if binary interaction parameters k_{ij} are be used,except for hydrogen.

The Harmens-Knapp Three-Parameter Cubic equation of State

The recent example of a fairly involved cubic equation of state is that of Harmens & Knapp(1980),of which a summary is in table 3.1. Their equation,reduces to several common cubic equations of state at particular values of

parameter c. Polynomial forms are

$$P = RT/(v-b)-a/(v^2+bcv-b^2(c-1)) \qquad (3.17)$$

$$v^3+(bc-b-RT/P)v^2+(a/P+b^2(1-2c)-bcRT/P)v$$

$$+b^3(c-1)+b^2(c-1)RT/P-ab/P = 0 \qquad (3.18)$$

Auxilliary parameters are $\beta=b/v_c$ and $\zeta = (P_c/RT_c)/v_c$. They were correlated in terms of acentric factor and reduced
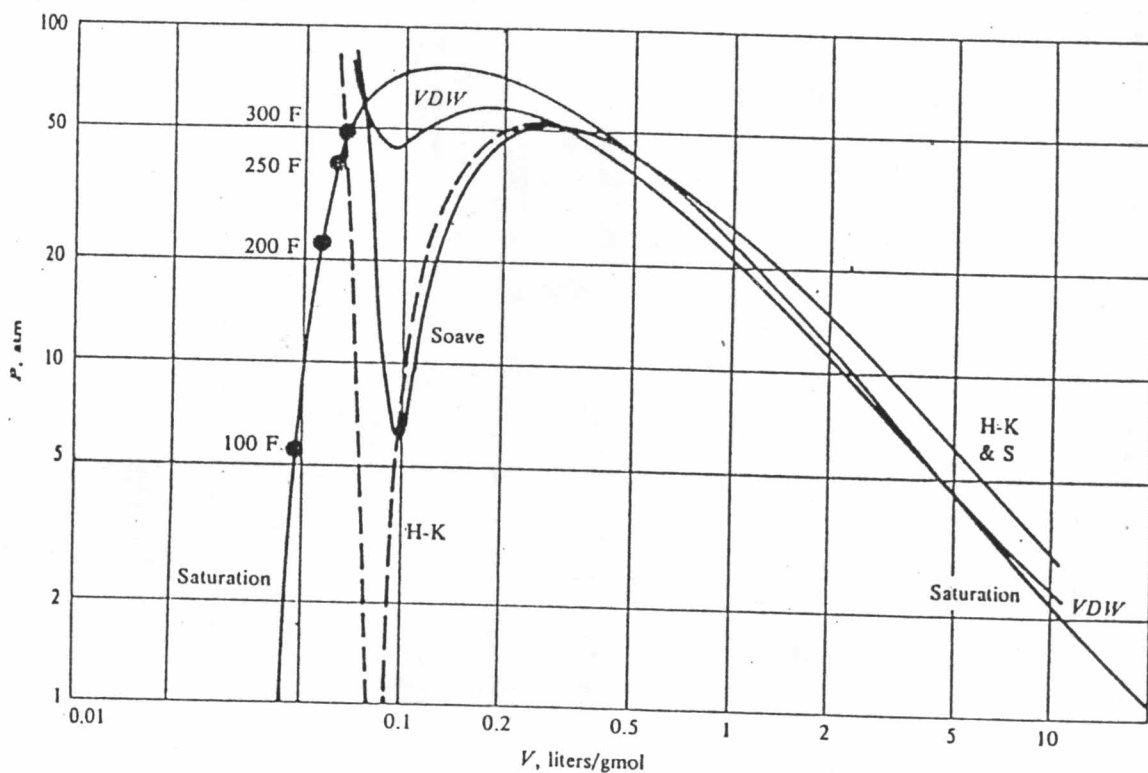

Figure 3.4 Plots of 250 F isotherms of sulfur dioxide with the Harmens-Knapp, Soave, and van der Waals equations, and comparison with the true saturation curve.

Table 3.1 The Harmens-Knapp Three-Parameter Cubic Equation of State (Harmens & Knapp 1980)

Standard form:

$$P = \frac{RT}{V - b} - \frac{a}{v^2 + bcV - b^2(c - 1)}$$ 3.19

Parameters:

$$\beta = 0.10770 + 0.76405\zeta - 1.24282\zeta^2 + 0.96210\zeta^3$$

$$\zeta = 0.3211 - 0.080\omega + 0.0384\omega^2$$

$$\Omega_a = 1 - 3\zeta + 3\zeta^2 + \beta\zeta(3 - 6\zeta + \beta\zeta)$$

$$\Omega_b = \beta\zeta$$

$$\alpha(T_r) = \left\{ 1 + A(1 - \sqrt{T_r}) - B\left(1 - \frac{1}{T_r}\right) \right\}$$

when $\omega \leq 0.2$,

$$A = 0.50 + 0.27767\omega + 2.17225\omega^2$$

$$B = -0.022 + 0.338\omega - 0.845\omega^2$$

when $\omega > 0.2$,

$$A = 0.41311 + 1.14657\omega$$

$$B = 0.0118$$

when $T_r > 1.0$,

$$\alpha(T_r) = 1.0 - (0.6258 + 1.5227\omega)\ln T_r + (0.1533 + 0.41\omega)(\ln T_r)^2$$

$$a = \alpha(T_r)\Omega_a \frac{R^2 T_c^2}{P_c'}$$ 3.20

$$b = \Omega_b \frac{RT_c}{p_c}$$ 3.21

$$c = 1 + \frac{1 - 3\zeta}{\beta\zeta}$$ 3.22

Fugacity coefficient and residual properties:

$$\ln \phi = z - 1 + \ln \frac{RT}{P(V - b)} - \frac{a}{RT}L$$ 3.23

$$H - H^{id} = PV - RT + \left(T\frac{da}{dT} - a\right) \cdot L$$

$$S - S^{id} = L\frac{da}{dT} - R\ln\frac{RT}{V - b} \quad (S^{id} \text{ is the entropy of ideal gas at } 1 \text{ atm})$$

$$K = \sqrt{c^2 + 4c - 4}$$

$$L = \frac{1}{Kb}\ln\frac{2V + b(c + K)}{2V + b(c - K)}$$

From Walas, S.M.

temperature by using critical isotherms and vapor pressure data of twenty substances ranging from argon to n-decane. In comparison with the Soave and Peng-Robinson equations, the new equation has superior performance for calculation of volumes along the critical isotherm, boiling temperature, and saturated liquid volumes the plots of figure 3.4 for sulfur dioxide at 250 °F shows that HK equation predicts the saturation pressure and volumes most closely. Though the equation is somewhat more complex than other cubics, there is some improvement in accuracy. The equation for calculation of mixture fugacity coefficient is

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B^*) + \frac{A^*}{B^* \sqrt{u^2 - 4w}} \left(\frac{b_i}{b} - \delta_i \right) \ln \frac{2Z + B^*(u + \sqrt{u^2 - 4w})}{2Z + B^*(u - \sqrt{u^2 - 4w})} \qquad 3.24$$

where
$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum_j y_j T_{cj}/P_{cj}}$$

$$\delta_i = \frac{2a_i^{1/2}}{a} \sum_j x_j a_j^{1/2}(1 - \bar{k}_{ij})$$

If all $\bar{k}_{ij} = 0$, this reduces to

$$\delta_i = 2 \left(\frac{a_i}{a} \right)^{1/2}$$

where u=c in (3.19) and w = 1-u,w in this equation different from acentric factor of Pitzer as defined before.

The Peng-Robinson Equation of State

Several goals were set by Peng & Robinson(1976)in developing a new two-parameter equation of state cubic in volume.

1. The parameter should be expressible in terms of P_c,T_c and acentric factor.

2. The model should result in improved performance in the vicinity of the critical point,particularly for calculations of Z_c and liquid density.

3. The mixing rules should not employ more than one binary interaction parameter,and that should be independent of temperature,pressure and composition.

4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

According to the Peng-Robinson(PR) equation the critical compressibility is Z_c=0.307,this value is nearer the true values of many substances,particularly non-polar ones,than are the Z_cs of some other two-parameter equation of state.This is a partial explanation of the fact, that the PR equation is able to predict liquid densities more acculately that does the Soave equation.Fugacity coefficients of both phases were found to be equally accurate with either the Soave or the PR equation.Peng-Robinson equation are shown

The Peng-Robinson Equation of State (Peng & Robinson 1976)

Standard form:

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

Parameters:

$a = 0.45724 R^2 T_c^2 / P_c$,

$b = 0.07780 R T_c / P_c$,

$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$,

$A = a\alpha P / R^2 T^2 = 0.45724 \alpha P_r / T_r^2$,

$B = bP / RT = 0.07780 P_r / T_r$.

Polynomial form:

$$z^3 - (1 - B) z^2 + (A - 3B^2 - 2B) z - (AB - B^2 - B^3) = 0.$$

Mixtures:

$a\alpha = \Sigma\Sigma y_i y_j (a\alpha)_{ij}$,

$b = \Sigma y_i b_i$,

$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j}$,

$A = \Sigma\Sigma y_i y_j A_{ij}$,

$B = \Sigma y_i B_i$,

$A_{ij} = (1 - k_{ij})(A_i A_j)^{0.5}$,

$k_{ii} = 0$.

Data of Katz & Firoozabadi (1978):

nitrogen + HC	$k_{ij} = 0.12$	
CO_2 + HC	0.15	
ethane + HC	0.01	
propane + HC	0.01	
methane +	ethane	0
	propane	0
	$nC4$	0.02
	$nC5$	0.02
	$nC6$	0.025
	$nC7$	0.025
	$nC8$	0.035
	$nC9$	0.035
	$nC10$	0.035
	$nC20$	0.054
	benzene	0.06
	cyclohexane	0.03

$$\ln \hat{\phi}_i = \frac{B_i}{B}(z - 1) - \ln(z - B) + \frac{A}{4.828B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j (a\alpha)_{ij}\right] \ln\left[\frac{z + 2.414B}{z - 0.414B}\right]$$

The Modified Soaved(Graboski & Daubert) Equation of State

Graboski & Daubert(1978)proposed a modification of the Soave-Redlich-Kwong equation of state which presented the finished form of the correlation for treating mixtures of hydrocarbons of importance to the natural gas and petroleum refining industries.The complete correlation is fully generalized,requiring only the readily available characterization parameters to make equilibruim calculations. The original Soave development was based on an accurate correlation of hydrocarbon vapor pressures in terms of reduced temperature,reduced pressure,and the acentric factor. By accurately correlating vapor pressure,the equation of state is capable of accurately predicting the fugacity of fluids and therefore the phase equilibrium behavior. Specifically,Soave used the critical point and the vapor pressure at a reduced temperature of 0.7 for a number of compounds to determine the function required to correlate vapor pressures.A limited set of critical pressures,critical temperatures,and acentric factors which are not totally consistent with the recommended American Petroleum Institute Data Book parameters are used in the original development. Thus,the Soave "α" equation was refit with the expanded property set.Instead of anchoring the equation at $T_r=0.7$, the regression was based on a detailed set of hydrocarbon vapor pressure data compiled by the Penn State API research

staff.

According to Soave,the term "α" is defined as

$$\alpha = (1+S(1-\sqrt{T_r}))^2 \qquad 3.27$$

where $S = a+bw+cw^2$

T_r = reduced temperature T/T_c

w = acentric factor

a,b,c = constant

The "α" function was determined as a function of reduced temperature and acentric factor for the API vapor pressure data set.It was found that equation (5) correlated the "α" data well.The regression equation for "S" based on the "α" data was derived to be

$$S = 0.48508 + 1.55171w - 0.15613w^2 \qquad 3.28$$

Standard form of modified SRK(Graboski & Daubert) equation of state

$$\ln \dot\phi_i = \frac{b_i}{b}(z-1) - \ln\left[z\left(1-\frac{b}{V}\right)\right] + \frac{a\alpha}{bRT}\left[\frac{b_i}{b} - \frac{2}{a\alpha}\sum_j y_j(a\alpha)_{ij}\right]\ln\left(1+\frac{b}{V}\right)$$
$$= \frac{B_i}{B}(z-1) - \ln(z-B) + \frac{A}{B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j(a\alpha)_{ij}\right]\ln\left(1+\frac{B}{z}\right) \qquad 3.29$$

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V + b)}$$ **3.30**

Parameters:

$a = 0.42747R^2 T_c^2/P_c$,

$b = 0.08664RT_c/P_c$,

$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_r^{0.5})]^2$,

$\alpha = 1.202 \exp(-0.30288T_r)$
   for hydrogen (Graboski & Daubert 1979),

$A = a\alpha P/R^2 T^2 = 0.42747\alpha P_r/T_r^2$,

$B = bP/RT = 0.08664P_r/T_r$

Polynomial forms:

$$V^3 - \frac{RT}{P}V^2 + \frac{1}{P}(a\alpha - bRT - Pb^2)V - \frac{a\alpha b}{P} = 0,$$

$$z^3 - z^2 + (A - B - B^2)z - AB = 0.$$ **3.31**

Partly reduced form

$$P_r = \frac{3T_r}{V_r - 0.2599} - \frac{3.8473\alpha}{V_r(V_r + 0.2599)}$$

Mixtures:

$a\alpha = \Sigma\Sigma y_i y_j (a\alpha)_{ij}$,

$b = \Sigma y_i b_i$,

$A = \Sigma\Sigma y_i y_j A_{ij}$,

$B = \Sigma y_i B_i$.

Cross-parameters:

$(a\alpha)_{ij} = (1 - k_{ij})\sqrt{(a\alpha)_i (a\alpha)_j}$,

$k_{ij} = 0$ for hydrocarbon pairs and hydrogen.