Generalized Partial Quantities from Pitzer's Expansion and Pseudocritical Rules

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It is often useful to be able to compute component partial quantities from properties of a mixture. We present in this note a general method to accomplish this for partial molal volumes, enthalpies, entropies, and Gibbs free energy or, more conveniently, the fugacity. The method is capable of being extended to other extensive thermodynamic properties.

If $\mathbf{B}$ were to represent an extensive property, and B the corresponding intensive property, then

$$\mathbf{B} = NB \tag{1}$$

Also, by definition, a partial quantity $\overline{B}_j$ is

$$\overline{B}_j \equiv (\partial \mathbf{B}/\partial N_j)_{T,P,N(j)} = B + N(\partial B/\partial N_j)_{T,P,N(j)} \tag{2}$$

The subscripting $N(j)$ simply means the moles of all components except $\mathbf{j}$ are to be held constant.

The key step in the derivation is to express the intensive property B, or a function of B, in terms of some generalized correlation. We have selected the so-called Pitzer expansion (*3*) since, as will be shown later, others have already obtained useful correlations which may be employed to obtain numerical results. For example, if $\mathbf{B}$ were to be the total system volume $\mathbf{V}$, then we would use as B, RTZ_m/P since the Pitzer expansion is

$$Z_m = Z^{(0)}(P_r, T_r) + \omega Z^{(1)}(T_r, P_r) \tag{3}$$

In other words, we want a function of B such that

$$B \text{ or } f(B) = f(T_r, P_r, \omega) \tag{4}$$

Assuming we can always employ Equation (4), then we may expand Equation (2) as

$$\overline{B}_j = B + N[(\partial B/\partial T_r)_{P_r,\omega}\psi_T + (\partial B/\partial P_r)_{T_r,\omega}\psi_P + (\partial B/\partial \omega)_{P_r,T_r}\psi_\omega] \tag{5}$$

The functions ψ_T, ψ_P, and ψ_ω are not functions of the property B. Rather, they depend only upon the pseudocritical rules chosen to calculate T_c, P_c, and ω for the mixture. More will be said about these pseudocritical rules later.

To illustrate Equation (5), again with the property of volume, with $B = RTZ_m/P$

TABLE 1. EXPRESSIONS FOR PARTIAL QUANTITIES

Enthalpy

$$\overline{H}_j - H_j^0 = (H_m - H_m^0)\,[1 - \psi_T/T_r] + RT_c\{(C_{pm} - C^0_{pm})\,\psi_T/R + (Z_m - Z_T)\,T_r\psi_P/P_r + [(H - H^0)/RT_c]^{(1)}\,\psi_\omega\}$$

Entropy

$$(\overline{S}_j - S_j^0)/R = (S_m - S_m^0)/R - \ln y_j + (C_{pm} - C_{pm}^0)\,\psi_T/RT_r + (1 - Z_T)\,\psi_P/P_r + (S_m - S_m^0)^{(1)}\,\psi_\omega/R$$

Fugacity

$$\ln(f_j/Py_j) = \ln(f_m/P) + (H_m - H_m^0)\,\psi_T/RT_cT_r^2 + (Z_m - 1)\,\psi_P/P_r + \ln(f/P)^{(1)}\,\psi_\omega$$

TABLE 2. PSEUDOCRITICAL FUNCTIONS

Kay's rule (*2*)

$$T_c = \sum_{i=1}^{n} y_iT_{ci} \equiv T_c\,(K)$$

$$P_c = \sum_{i=1}^{n} y_iP_{ci} \equiv P_c\,(K)$$

$$\omega = \sum_{i=1}^{n} y_i\omega_i \equiv \omega\,(K)$$

$$\psi_T = T\,[T_c\,(K) - T_{cj}]/[T_c\,(K)]^2$$

$$\psi_P = P\,[P_c\,(K) - P_{cj}]/[P_c\,(K)]^2$$

$$\psi_\omega = \omega_j - \omega(K)$$

Modified Prausnitz-Gunn (*4*)

$$T_c = T_c\,(K)$$

$$P_c = Z_{cm}RT_c\,(K)/V_c\,(K) \equiv P_c\,(PG)$$

$$V_{cm}\,(K) = \sum_{i=1}^{n} y_iV_{ci}$$

$$\omega = \omega\,(K)$$

$$Z_{cm}\,(K) = \sum_{i=1}^{n} y_iZ_{ci}$$

ψ_T = same as Kay's rule

$$\psi_P = [P/P_c\,(PG)]\,\{[(V_{cj} - V_c\,(K))/V_c\,(K)] - [(Z_{cj} - Z_c\,(K))/Z_c\,(K)] - [(T_{cj} - T_c\,(K))/T_c\,(K)]\}$$

ψ_ω = same as Kay's rule

Joffee-Stewart-Burkhardt-Voo (*1, 7*)

$$T_c = L^2/J \equiv T_c\,(\text{JSBV})$$

$$P_c = T_c\,(\text{JSBV})/J \equiv P_c\,(\text{JSBV})$$

$$L = \left[\sum_{i=1}^{n} (y_iT_{ci})/(P_{ci})^{1/2}\right]$$

$$J = (1/8)\sum_{i=1}^{n}\sum_{k=1}^{n} y_iy_k\,[(T_{ci}/P_{ci})^{1/3} + T_{ck}/P_{ck})^{1/3}]^3$$

$$\psi_T = 2\,[T/T_c\,(\text{JSBV})]\left[Q_j \Big/ \sum_{i=1}^{n} y_iQ_i - R_j \Big/ \sum_{i=1}^{n} y_iR_i\right]$$

$$\psi_P = [P/P_c\,(\text{JSBV})]\,\psi_T/[T/T_c\,(\text{JSBV})]$$

$$Q_j = \sum_{k=1}^{n} y_j\,[(T_{cj}/P_{cj})^{1/3} + (T_{ck}/P_{ck})^{1/3}]^3$$

$$R_j = T_{cj}/P_{cj}^{1/2}$$

ψ_w = same as Kay's rule

Redlich-Kwong (*5*)

$$T_r^{-2.5}P_c^{-1} = \sum_{i=1}^{n} y_i(T_{ri}^{-2.5}P_{ci}^{-1})$$

$$(T_rP_c)^{-1} = \sum_{i=1}^{n} y_i(T_{ri}P_{ci})^{-1}$$

$$\psi_T = (2/3)T_r^{-1}\{(T_{rj}P_{cj})^{-1}\,(T_r^{-2.5}P_c^{-1}) - (T_{rj}^{-2.5}P_{cj}^{-1})(T_r^{-1}P_c^{-1})\}\,(T_r^{2.5}P_c)^2$$

$$\psi_P = PT_r\,[(T_{rj}P_{cj})^{-1} - (T_rP_c)^{-1}]$$

ψ_ω = same as Kay's rule

TABLE 3. SUMMARY OF RESULTS

20% ethane, 80% methane mixture at 70°F., 2,000 lb./sq.in.abs. (8)
Calculated by using pseudocritical rule of

	Expt. (8)	Kay	MP-G†	R-K**	J-S-B-V††
I. Thermodynamic quantities					
Z_{mix}	0.728	0.755	0.754	0.724	0.755
$\overline{V}_{CH_4}$ (cu. ft./lb. mole)	2.29	2.305	2.300	2.31	2.35
$\overline{V}_{C_2H_6}$ (cu. ft./lb. mole)	0.39	0.998	0.947	0.205	0.568
V_{mix} (cu. ft./lb. mole)	2.068	2.152	2.131	2.064	2.141
$(\overline{H} - H^0)^*_{CH_4}$ (B.t.u./lb. mole)	−925	−967	−873	−870	−954
$(\overline{H} - H^0)_{C_2H_6}$ (B.t.u./lb. mole)	−3,690	−3,165	−3,120	−4,910	−3,200
II. Functions					
ω_{mix}		0.024	0.024	0.024	0.024
T_r		1.444	1.444	1.392	1.439
P_r		2.974	2.960	2.860	2.946
Z_T		1.650	1.649	1.857	1.650
Z_P		0.817	0.816	0.798	0.817
$\psi_{T(CH_4)}$		0.094	0.094	0.108	0.123
$\psi_{T(C_2H_6)}$		−0.714	−0.714	−0.818	−0.930
$\psi_{P(CH_4)}$		0.020	0.027	−0.163	0.252
$\psi_{P(C_2H_6)}$		−0.163	−0.243	1.210	−1.904
$\psi_{\omega(CH_4)}$		−0.011	−0.011	−0.011	−0.011
$\psi_{\omega(C_2H_6)}$		0.081	0.081	0.081	0.081

* Datum: $H = 0$ for pure liquid at −200°F.
† Modified Prausnitz-Gunn.
** Mixture rule from original Redlich-Kwong equation of state.
†† Joffe-Stewart, Burkhardt, and Voo.

$$\overline{V}_j = (RT/P)\,[Z_m + (Z_T - Z_m)\psi_T/T_r + (Z_m - Z_P)\,\psi_P/P_r + Z^{(1)}\,\psi_w] \quad (6)$$

Z_m is found from Equation (3) with the $Z^{(0)}$ and $Z^{(1)}$ functions from reference 3. The Z_T and Z_P terms have been expressed as a function of T_r, P_r, and ω (6). Again, the ψ functions depend only upon the pseudocritical rules chosen.

The equation for $\overline{V}_j$ is given in Equation (6). Comparable expressions for enthalpy, entropy, and fugacity are given in Table 1. In Equation (6) and Table 1, V_m, $(H_m - H_m{}^0)$, $(S_m - S_m{}^0)$, and $\ln(f_m/P)$ are available as functions of T_r, P_r and ω (1, 3).

Only four different pseudocritical rules were considered here, that is, those of Kay (2), modified Prausnitz-Gunn (4), Joffe-Stewart-Burkhardt-Voo (1, 7), and Redlich-Kwong (5). The ψ functions for these four rules are given in Table 2. Other ψ functions may easily be derived for different pseudocritical rules.

The relations given in Equation (6) with Tables 1 and 2 were tested on several systems. The results for a mixture containing 80 mole % methane, 20 mole % ethane at 70°F., 2,000 lb./sq.in.abs. are shown in Table 3. The Joffe-Stewart-Burkhardt-Voo rule, in general, gave the least error, though none predicted the partial molal volume of ethane very accurately.

Other tests also indicated that of the pseudocritical rules tested, the J-S-B-V rules were generally more reliable.

The relations given in Tables 1 and 2 form a convenient way to estimate partial molal quantities providing a suitable mixture generalized correlation, such as the Pitzer expansion form, is applicable and providing a pseudocritical formulation is possible.

NOTATION

B = intensive thermodynamic property
$\mathbf{B}$ = extensive thermodynamic property = BN
f = fugacity
H = enthalpy
N = total moles; N_j, moles of j
P = pressure
S = entropy
T = temperature
V = volume
y = mole fraction
Z = compressibility factor
Z_P = $Z - P_r\,(\partial Z/\partial P_r)_{T_r}$
Z_T = $Z + T_r\,(\partial Z/\partial T_r)_{P_r}$
ω = acentric factor
ψ_P = $N\,(\partial P_r/\partial N_j)_{T,P,N(j)}$
ψ_T = $N\,(\partial T_r/\partial N_j)_{T,P,N(j)}$
ψ_ω = $N\,(\partial \omega_m/\partial N_j)_{T,P,N(j)}$

Subscripts

c = critical
m = mixture
r = reduced

Superscript

0 = ideal gas state at 1 atm.

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