(40), and (41) are similar to the usual well-known equations when only thermal, compression, and mass transfer effects are involved, but these extended equations account for other effects such as surface tension, tensile stress, electric polarization, and magnetic polarization. The proper way to handle gravitation and other field effects has been shown and contrasted with the erroneous methods in three well-known books.

For a more complete discussion of this subject the reader is referred to the previous extensive treatment of The Symmetrical Fundamental Property Relation of Thermodynamics [5]. ☐

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NOMENCLATURE

C	Velocity of light
E	Total energy (internal + kinetic + potential of all kinds)
ϵ	Electrical potential or field
F	Force
G	Gibbs free energy, U + PV − TS, or G = U + PV − TS − $\gamma\alpha$ − Fl − ϵP − HM
g	Acceleration due to gravity
H	Enthalpy, U + PV
H	Magnetic potential or field
l	Length
LW	Lost work (irreversibility)
M	Molecular weight
M	Magnetic polarization
m	Mass
n	Number of moles
P	Pressure
P	Electrical polarization
Q	Heat flow
S	Entropy
T	Temperature (absolute)
U	Internal (intrinsic) energy of matter
u	Velocity
V	Volume
W	Work flow
Z	Height above a reference point
α	Surface area
δ	Quantity transferred (as heat δQ and work δW)
γ	Surface tension
Φ	Potential energy (gz in gravitational field)
μ	Chemical or mass potential ($\mu_i = \overline{G}_i$)

Superscript

—	Denotes partial extensive property
α,β	Points in gravitation field

Subscripts

i	Denotes different chemical species
j	Denotes all chemical species except particular one i being examined.

RESIDUAL FUNCTIONS AND FUGACITY

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TWO PROPERTIES WHICH generate considerable confusion in thermodynamics courses are residual functions and fugacity. They are, in fact, closely related concepts and, in this paper, we have developed them in a consistent manner. In this way, the composition dependence of the fugacity coefficient of a component in a mixture appears in an unambiguous manner.

PROPERTY CHANGES

The property changes which we shall develop in this paper are all of the form: real fluid property less perfect gas property. The difference is either at the same temperature and pressure or at the same temperature and density. The definitions are (using M to denote U, H, A, G, S, V).

$$M^r \equiv M(T,\rho) - M^*(T,\rho) \tag{1}$$

$$M^R \equiv M(T,P) - M^*(T,P) \tag{2}$$

$$\begin{aligned} M - M_r^* &\equiv M(T,P) - M^*(T,P_o) \\ &\equiv M(T,\rho) - M^*(T,P_o/RT) \end{aligned} \tag{3}$$

$$\begin{aligned} M - M_o^* &\equiv M(T,P) - M^*(T_o,P_o) \\ &\equiv M(T,\rho) - M^*(T_o,P_o/RT_o) \end{aligned} \tag{4}$$

We choose to develop these expressions in the T-ρ plane because the results are then most convenient for computer computation. The path is

$$M(T,\rho) \rightarrow M^*(T,0) \rightarrow M^*(T,\rho)$$

where the real fluid and perfect gas planes intersect at zero density.

The most useful working equations for this development are

$$\begin{aligned} dU &= c_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \\ &= c_V dT + R\left(\frac{\partial Z}{\partial(1/T)}\right)_\rho \frac{d\rho}{\rho} \end{aligned} \tag{5}$$

$$dA = -S\,dT - P\,dV = -S\,dT + RTZ\frac{d\rho}{\rho} \tag{6}$$

We have introduced the compressibility factor to facilitate equation of state use. Integrating these expressions along the chosen paths provides

$$\begin{aligned} &U(T,\rho) - U^*(T,\rho) \\ &\quad = U(T,\rho) - U^*(T,0) \rightarrow R\int_0^\rho \left(\frac{\partial Z}{\partial(1/T)}\right)_\rho \frac{d\rho}{\rho} \\ &\qquad + U^*(T,0) - U^*(T,\rho) \rightarrow 0 \end{aligned}$$

$$\begin{aligned} &A(T,\rho) - A^*(T,\rho) \\ &\quad = A(T,\rho) - A^*(T,0) \rightarrow RT\int_0^\rho Z\frac{d\rho}{\rho} \\ &\qquad + A^*(T,0) - A^*(T,\rho) \rightarrow -RT\int_0^\rho \frac{d\rho}{\rho} \end{aligned}$$

Thus, the residual functions, in dimensionless form, are

$$\frac{U^r}{RT} = \frac{1}{T}\int_0^\rho \left(\frac{\partial Z}{\partial(1/T)}\right)_\rho \frac{d\rho}{\rho} \tag{7}$$

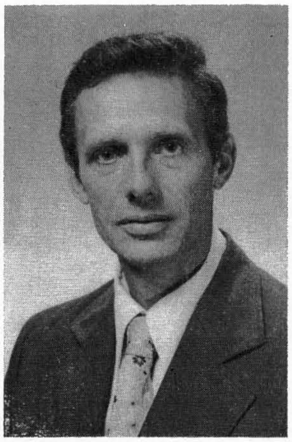
$$\frac{A^r}{RT} = \int_0^\rho [Z - 1]\frac{d\rho}{\rho} \tag{8}$$

Of course, the other residual functions are combinations of these two

$$\frac{H^r}{RT} = \frac{U^r}{RT} + \frac{PV - PV^*}{RT} = \frac{U^r}{RT} + Z - 1 \tag{9}$$

$$\frac{S^r}{R} = \frac{U^r}{RT} - \frac{A^r}{RT} \tag{10}$$

$$\frac{G^r}{RT} = \frac{A^r}{RT} + \frac{PV - PV^*}{RT} = \frac{A^r}{RT} + Z - 1 \tag{11}$$



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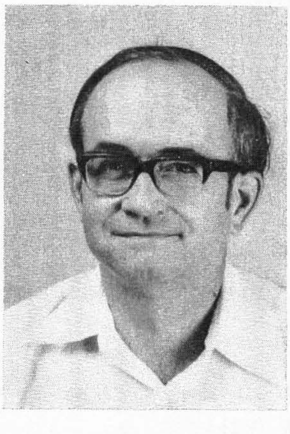

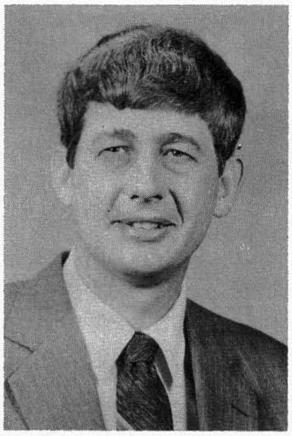

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A consistant development of residual functions, property changes and fugacity reveals close relationships among the various properties.

By definition, V^r is zero so

$$\frac{PV^r}{RT} = 0 \qquad (12)$$

To convert these results to residual functions in the T-P plane requires only adjustment of the perfect gas values

$$M(T,P) - M^*(T,P)$$
$$= M(T,\rho) - M^*(T,\rho) + M^*(T,\rho) - M^*(T,P/RT) \quad (13)$$

where the required terms are

$$M(T,\rho) - M^*(T,\rho) = M^r \qquad (1)$$

$$M^*(T,\rho) - M^*(T,P/RT) = \begin{cases} 0 \text{ if } M \text{ is } U,H \\ -\ell n\ Z \text{ if } M \text{ is } A,G,-S \end{cases} \qquad (14)$$

This step is equivalent to rederiving the expressions in a T-P plane.

The other types of property change (Eqs. 3 and 4) also require only adjustments of the perfect gas values. For Eq. 3, the adjustment is

$$M - M_r^* = M(T,\rho) - M^*(T,\rho)$$
$$+ M^*(T,\rho) - M^*(T,P_o/RT) \qquad (3)$$

where

$$M(T,\rho) - M^*(T,\rho) = M^r$$

$$M^*(T,\rho) - M^*(T,P_o/RT) = \begin{cases} 0 \text{ if } M \text{ is } U,H \\ -\ell n\ Z + \ell n \dfrac{P}{P_o} \\ \qquad \text{if } M \text{ is } A,G,-S \end{cases} \qquad (15)$$

Eq. 4 bases the property change upon the standard state and the adjustment is

$$M - M_o^* = M(T,\rho) - M^*(T,\rho)$$
$$+ M^*(T,\rho) - M^*(T,P_o/RT)$$
$$+ M^*(T,P_o/RT) - M^*(T_o,P_o/RT)$$
$$+ M^*(T_o,P_o/RT) - M^*(T_o,P_o/RT_o) \qquad (4)$$

In this case, it is most convenient to establish U-U$_o$* and S-S$_o$* and then calculate the others from these two. Utilizing Eq. 4, the changes are

$$\frac{U - U_o^*}{RT} = \frac{U - U_r^*}{RT} + \frac{1}{T}\int_{T_o}^{T} \frac{C_V^*}{R}\, dT \qquad (16)$$

$$\frac{S - S_o^*}{R} = \frac{S - S_r^*}{R} - \ell n \frac{T}{T_o} \int_{T_o}^{T} \frac{C_V^*}{R}\frac{dT}{T} \qquad (17)$$

and the other functions become

$$\frac{H - H_o^*}{RT} = \frac{U - U_o^*}{RT} + \frac{PV - RT_o}{RT} = \frac{U - U_o^*}{RT} + Z - \frac{T_o}{T} \quad (18)$$

$$\frac{A - A_o^*}{RT} = \frac{U - U_o^*}{RT} - \frac{TS - T_oS_o^*}{RT}$$
$$= \frac{U - U_o^*}{RT} - \frac{T[S - S_o^*]}{RT} - \frac{S_o^*[T - T_o]}{RT}$$
$$= \frac{U - U_o^*}{RT} - \frac{S - S_o^*}{R} - \frac{S_o^*}{R}\left(1 - \frac{T_o}{T}\right) \qquad (19)$$

$$\frac{G - G_o^*}{RT} = \frac{H - H_o^*}{RT} - \frac{S - S_o^*}{RT} - \frac{S_o^*}{R}\left(1 - \frac{T_o}{T}\right) \qquad (20)$$

It is also very important to note that throughout these equations the only integrals required are

$$\frac{1}{T}\int_0^{\rho} \left(\frac{\partial Z}{\partial(1/T)}\right)_{\rho} \frac{d\rho}{\rho} = \frac{U^r}{RT}$$

$$\int_0^{\rho} [Z - 1] \frac{d\rho}{\rho} = \frac{A^r}{RT}$$

$$\frac{1}{T}\int_{T_o}^{T} \frac{C_V^*}{R}\, dT$$

$$\int_{T_o}^{T} \frac{C_V^*}{R}\frac{dT}{T}$$

The first two integrals are relatively simple applications of the equation of state, and the latter two integrals involve only perfect gas specific heat.

One last point to note is the T-P plane derivation of G^R/RT. Again followiing a constant temperature path from P → O → P produces

$$G(T,P) - G^*(T,P)$$
$$= G(T,P) - G^*(T,0) + G^*(T,0) - G^*(T,P)$$

but the fundamental equation for G is

$$dG = - S\ dT + V\ dP = - S\ dT + RTZ\,\frac{dP}{P} \qquad (21)$$

and the value for G^R becomes

$$G(T,P) - G^*(T,P) = RT\int_0^P Z\,\frac{dP}{P} - RT\int_0^P \frac{dP}{P}$$

Therefore, the final expression is

$$\frac{G^R}{RT} = \int_0^P [Z - 1]\,\frac{dP}{P} = \frac{A^r}{RT} + Z - 1 - \ell n\ Z \qquad (22)$$

FUGACITY

The usual definition for fugacity (of a pure component) is, in differential form

$$dG_i = RT\ d\ \ell n\ f_i \quad @\ \text{constant}\ T$$

$$\lim_{P\to0}\frac{f_i}{P} = 1.0 \qquad (23)$$

Upon integration, this expression becomes

$$\int_{G_i^*}^{G_i} dG_i = RT\int_{\ell n\ P}^{\ell n\ f_i} d\ \ell n\ f_i$$

$$G_i(T,P) - G_i^*(T,P) = RT\ \ell n\,\frac{f_i}{P} = G_i^R \qquad (24)$$

Eq. 24 has an obvious relationship with Eq. 22. In fact, we might as well have defined fugacity with these two expressions and have extended the definition to mixtures and components in mixtures:

$$\ell n\,\frac{f_i}{P} \equiv \frac{G_i(T,P) - G_i^*(T,P)}{RT} = \frac{G_i^R}{RT} \qquad (25)$$

$$\ell n\,\frac{f_m}{P} \equiv \frac{G_m(T,P) - G_m^*(T,P)}{RT} = \frac{G_m^R}{RT} \qquad (26)$$

$$\ell n\,\frac{\hat{f}_i}{P} \equiv \frac{\bar{G}_i(T,P) - G_i^*(T,P)}{RT} \qquad (27)$$

Eq. 22 reveals the calculation procedure for Eqs. 25 and 26. Evaluation of Eq. 27 requires closer examination

$$\frac{\bar{G}_i - G_i^*}{RT} = \frac{\bar{G}_i - G_i}{RT} + \frac{G_i - G_i^*}{RT} \qquad (28)$$

Evaluation of Eq. 28 requires the following analysis

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,Z}$$

$$\left(\frac{\partial[\bar{G}_i - G_i]}{\partial P}\right)_{T,z} = \bar{V}_i - V_i$$

$$\left.\frac{\bar{G}_i - G_i}{RT}\right|_{P=0}^{P=P} = \int_0^P \frac{\bar{V}_i - V_i}{RT}\,dP$$

$$\lim_{P\to0}\frac{\bar{G}_i - G_i}{RT} = \frac{\bar{G}_i^* - G_i^*}{RT} = \ell n\ z_i \quad \text{(ideal solution)}$$

$$\frac{\bar{G}_i - G_i}{RT} = \ell n\ z_i + \int_0^P \frac{\bar{V}_i - V_i}{RT}\,dP \qquad (29)$$

$$\frac{G_i - G_i^*}{RT} = \int_0^P [Z_i - 1]\,\frac{dP}{P} = \int_0^P \left(\frac{V_i}{RT} - \frac{1}{P}\right) dP \qquad (22)$$

Eq. 27 thus becomes

$$\ell n\,\frac{\hat{f}_i}{P} = \ell n\ z_i + \int_0^P \frac{\bar{V}_i - V_i}{RT}\,dP - \int_0^P \left(\frac{V_i}{RT} - \frac{1}{P}\right) dP$$

$$\ell n\,\frac{\hat{f}_i}{z_i P} = \int_0^P \left(\frac{\bar{V}_i}{RT} - \frac{1}{P}\right) dP \qquad (30)$$

Furthermore, utilizing previous relationships

$$\frac{\bar{G}_i - \bar{G}_i^*}{RT} = \frac{\bar{G}_i^R}{RT} = \frac{\bar{G}_i - G_i^*}{RT} - \frac{\bar{G}_i^* - G_i^*}{RT}$$

$$\ell n\,\frac{\hat{f}_i}{z_i P} = \frac{\bar{G}_i^R}{RT} \qquad (31)$$

It is also true that

$$\frac{\bar{G}_i^R}{RT} = \frac{\bar{G}_i^r}{RT} - \ell n\ Z_m$$

$$\frac{G_i^r}{RT} = \left(\frac{\partial(nA^r/RT)}{\partial n_i}\right)_{T,nV,n_{j\neq i}}$$

$$= \int_{nV}^{\infty} \left\{ \left(\frac{\partial(nZ_m)}{\partial n_i}\right)_{T,nV,n_{j\neq i}} - 1 \right\} \frac{d(nV)}{nV}$$

CONCLUSIONS

A consistent development of residual functions, property changes and fugacity reveals close relationships among the various properties. The composition dependence of the fugacity coefficient of a component in a solution is unambiguous. All properties result from integrals which are easy to derive from good equations of state. □

NOMENCLATURE

A —Helmholz function
C_V^* —perfect gas specific heat (constant volume)
f_i —fugacity of pure i
f_m —fugacity of a mixture
$\hat{f}_i$ —fugacity of component i in a mixture
G —Gibbs function
H —enthailpy
M —general property symbol
n —number of moles
P —pressure
R —gas constant
S —entropy
T —temperature
U —internal energy
V —molar volume
nV —total volume
Z —compressibility factor
z —mole fraction
ρ —density

Superscripts

^{r} —T-ρ residual
^{R} —T-P residual
* —perfect gas
$\bar{}$ —partial molar

Subscripts

$_i$ —component i
$_m$ —mixture
$_o$ —standard state
$_r$ —reference state

A GRAPHIC LOOK AT AVAILABILITY FUNCTIONS

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THE THERMODYNAMIC availability functions can be viewed graphically, and this view provides valuable unexpected insights into the nature and meaning of the functions.

To demonstrate, consider the question, "What is the maximum work a system can perform in moving into equilibrium with the temperature and pressure of its environment?"

The answer is given graphically in Fig. 1. Maximum work is the work performed when moving reversibly along paths (1→2) and (2→e), from an arbitrary initial state (1) to a final state (e) in equilibrium with the environment.

Now this may appear to be an arbitrary choice of paths; but it is not. It constitutes a unique combination of reversible paths leading from (1) to (e), that allow heat and mass transfer to occur only when the system is at the potentials of its environment. These are paths that take the system *isentropically and at constant molarity,* (1→2), to the temperature of that environment; and then isothermally, (2→e), to the chemical potential of the environment. And it is rather easy to prove, again graphically, that no combination of reversible process paths connecting states (1) and (e), can produce more work.

PROOF

Curve (1-k-e) in Fig. 1 traces a reversible but arbitrary process path taking a system from state