

*Dedicated to Professor Ion PĂVĂLOIU on his 60<sup>th</sup> anniversary*

## LIMITING CASES OF THERMODYNAMIC FUNCTIONS

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**Abstract.** Calculations necessary in thermodynamics and especially in phase equilibria require knowledge of the function  $P(V,T)$  (pressure-volume-temperature) for each fluid & fluid mixture. Another important function is  $\gamma(T,x)$  of the activity coefficient in the liquid phase related to the temperature & composition. Limiting cases of these functions also considering their interrelationship provide important information for their range of application and validity which are difficult to be assessed otherwise.

## THERMODYNAMIC FUNCTIONS

Among the various  $P(V, T)$  relations we will consider for this discussion the SRK EoS (Equation of State) first proposed by Soave (1972):

$$P = \frac{-\alpha}{V(V+b)} + \frac{RT}{V-b} \quad (1)$$

(where  $\alpha$  = energy parameter,  $b$  = co-volume,  $R$  = gas constant)

The key auxiliary quantity in applied thermodynamics is the fugacity coefficient defined for a pure substance defined by the integral:

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$$\ln \Phi = \frac{1}{RT} \int_0^P \left( V - \frac{RT}{P} \right) dP \quad (2)$$

To solve the integral of equation (2) a function  $V(P,T)$  is required but most EoS are, as in (1), given as  $P(V,T)$ . Equation (2) can be equivalently written as:

$$\ln \Phi = (z-1) - \ln z - \frac{1}{RT} \int_z^{\infty} \left( P - \frac{RT}{V} \right) dV \quad (3)$$

where  $z = \frac{PV}{RT}$  is the compressibility factor.

Entering (1) in (3) and solving the integral we get for SRK:

$$\ln \Phi_i = \left( \frac{PV_i}{RT} - 1 \right) - \ln \left[ \frac{P(V_i - b_i)}{RT} \right] - \frac{\alpha_i}{b_i RT} \ln \left( \frac{V_i + b_i}{V_i} \right) \quad (4)$$

Complete knowledge of phase equilibria, key issue in applied thermodynamics, over a range of temperature, pressure and composition is provided if we know  $\hat{O}$  for each compound **in a mixture** defined as:

$$\ln \hat{\Phi}_i = z - 1 - \ln z - \int_z^{\infty} \left( \frac{\partial z}{\partial n_i} \Big|_{T,V,n_j} - 1 \right) \frac{dV}{V} \quad (5)$$

To solve the integral of equation (5) we need, in addition to a function such as equation (1), a relation for the parameters  $a$  and  $b$  of the mixture. A well-known relation used is (van der Waals one fluid mixing rules):

$$a = \sum_i \sum_j x_i x_j \alpha_{ij} \quad , \quad b = \sum_i x_i b_i \quad (6)$$

(all parameters without  $i$  correspond to mixture)

Entering (6) in (5) yields:

$$\ln \hat{\Phi}_i = \frac{b_i}{b} \left( \frac{PV}{RT} - 1 \right) - \ln \left[ \frac{P(V-b)}{RT} \right] - \frac{\alpha}{bRT} \left( \frac{2 \sum_j x_j \alpha_{ji}}{\alpha} - \frac{b_i}{b} \right) \ln \left( 1 + \frac{b}{V} \right) \quad (7)$$

With this information, two important functions - related to each other and the non-ideality of, especially, the liquid phase - can be estimated. These are the excess Gibbs Free Energy and the activity coefficient:

Excess Gibbs Free Energy:

$$\frac{g^E}{RT} = \ln \Phi - \sum_i x_i \ln \Phi_i = \sum_i x_i \ln \gamma_i \quad (8)$$

$$\ln \gamma_i = \frac{\partial}{\partial n_i} \left( \frac{ng^E}{RT} \right)_{T,P,n_j} = \ln \frac{\hat{\Phi}_i}{\Phi_i}$$

From equations (8) and (4) we have for  $g^E$  after some algebra:

$$\begin{aligned} \frac{g^E}{RT} = & \sum_i x_i \ln \left[ \frac{P(V_i - b_i)}{RT} \right] - \ln \left[ \frac{P(V - b)}{RT} \right] + \frac{P}{RT} (V - \sum_i x_i V_i) - \\ & - \frac{1}{RT} \left[ \frac{\alpha}{b} \ln \left( \frac{V + b}{V} \right) - \sum_i x_i \frac{\alpha_i}{b_i} \ln \left( \frac{V_i + b_i}{V_i} \right) \right] = \\ & \sum_i x_i \ln \left[ \frac{(V_i - b_i)}{V - b} \right] + \frac{P}{RT} (V - \sum_i x_i V_i) - \frac{1}{RT} \left[ \frac{\alpha}{b} \ln \left( \frac{V + b}{V} \right) - \sum_i x_i \frac{\alpha_i}{b_i} \ln \left( \frac{V_i + b_i}{V_i} \right) \right] \end{aligned} \quad (9)$$

From equations (8), (4), and (7) we get for - the more 'sensitive' property -  $\gamma_i$ :

$$\begin{aligned} \ln \gamma_i = & \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} = \\ \ln \gamma_i = & \left[ \ln \left( \frac{V_i - b_i}{V - b} \right) + \frac{b_i}{b} \left( \frac{PV}{RT} - 1 \right) + \left( 1 - \frac{PV_i}{RT} \right) \right] + \\ & + \left[ \frac{\alpha_i}{b_i RT} \ln \left( 1 + \frac{b_i}{V_i} \right) - \frac{\alpha}{b RT} \left( \frac{2 \sum_j x_j \alpha_j}{\alpha} - \frac{b_j}{b} \right) \ln \left( 1 + \frac{b}{V} \right) \right] \end{aligned} \quad (10)$$

Entering P from equation (1) into equation (10) we get after extensive but relatively simple algebra:

$$\ln \gamma_i = \left[ \ln \left( \frac{V_i - b_i}{V - b} \right) + 1 - \left( \frac{V_i - b_i}{V - b} \right) \right] +$$

$$+ \left[ \frac{\alpha V_i}{V(V+b)RT} - \frac{\alpha b_i}{b(V+b)RT} + \frac{\alpha_i}{b_i RT} \ln \left( 1 + \frac{b_i}{V_i} \right) - \frac{\alpha}{bRT} \left( \frac{2 \sum_j x_j \alpha_j}{\alpha} - \frac{b_i}{b} \right) \ln \left( 1 + \frac{b}{V} \right) \right] \quad (11)$$

For complex systems e.g. mixtures with electrolytes, polymers, polar fluids many explicit  $\gamma(T, x)$  functions have been proposed in the literature for describing phase equilibria. These  $\gamma(T, x)$  functions are usually preferred over cubic EoS such as equation (1) which, in the typical case, are valid only for non-polar systems. However, cubic EoS are most useful since they provide a full P-V-T relation. Furthermore, it is not clear whether their limitations are due to their functional form or the nature of the mixing and combining rules employed. The  $\gamma$ -model and the  $g^E$ -model as derived from a cubic EoS offer an approach which is capable of providing insight on the actual range of applicability of cubic EoS. To achieve this we will consider a number of limiting cases.

## LIMITING CASES

### a) Infinite Pressure Limit of $g^E$

From equations (1) and (9) if  $P \rightarrow \infty$ , the infinite pressure limits of the various terms of eq. (9) can be calculated as follows:

$$\lim_{P \rightarrow \infty} \left[ \ln \frac{P(V-b)}{RT} \right]^{eq(1)} = \lim_{P \rightarrow \infty} \left[ \ln \left[ 1 - \frac{\alpha(V-b)}{V(V+b)RT} \right] \right] - \ln 1 = 0 \quad (12)$$

since  $\lim_{P \rightarrow \infty} V = b$  and  $\lim_{P \rightarrow \infty} V_i = b_i$

$$\lim_{P \rightarrow \infty} \left[ \frac{PV}{RT} - \frac{P}{RT} \sum x_i V_i \right] = \quad (13)$$

$$\lim_{P \rightarrow \infty} \left\{ \frac{P(V-b)}{RT} + \frac{Pb}{RT} - \sum x_i \left[ \frac{P(V_i - b_i)}{RT} + \frac{Pb_i}{RT} \right] \right\} = \frac{P}{RT} (b - \sum x_i b_i) = 0$$

if we assume that equation (6) is used as mixing rule for the co-volume parameter.

Thus at  $P \rightarrow \infty$  equation (9) becomes:

$$\frac{g^{E,\infty}}{RT} = -\frac{1}{RT} \frac{\alpha}{b} \ln 2 - \sum \frac{x_i \alpha_i}{RT b_i} \ln 2 \Rightarrow \alpha = b \left( \sum x_i \frac{\alpha_i}{b_i} - \frac{g^{E,\infty}}{RT \ln 2} \right) \quad (14)$$

Equation (14) could be employed in many ways. For instance, if we have an external function of  $g^{E,\infty}$  we may use it as a mixing rule while for those systems where it may be assumed that  $g^{E,\infty} = 0$  such as alkane solutions equation (14) may yield the following simple mixing rule for the ratio of the energy versus the co-volume parameter:

$$\frac{\alpha}{b} = \sum x_i \frac{\alpha_i}{b_i} \quad (15)$$

Note that no mixing rule assumption entered in equation (9). Equation (15) may be proved to be a satisfactory substitute of the energy mixing rules given in equation (6). Indeed in a recent publication by Kontogeorgis & Vlamos (1998) it was showed that equation (15) yields very satisfactory results for phase equilibria calculations for asymmetric alkane systems.

#### ***b) Zero pressure limit of $g^E$***

Taking the zero pressure limit of equation (9) and upon assuming a relation for the ration  $\frac{V}{b} = U$ , justified by recent studies eg. Orbey & Sandler (1996), a similar to equations (14) or (15), mixing rule may be obtained:

$$\frac{\alpha}{bRT} = \frac{1}{-U} \left( \frac{g^{E,0}}{RT} - \sum x_i \ln \frac{b_i}{b} \right) + \sum x_i \frac{\alpha_i}{b_i RT} \quad (16)$$

*c) Zero concentration range limit of  $\gamma_i$*

$\gamma_i^\infty = \lim_{x_i \rightarrow 0} \gamma_i$  is called the infinite-dilution activity coefficient.

Taking this limit in equation (11) we get:

$$\ln \gamma_i^\infty = \ln \left( \frac{V_1 - b_1}{V_2 - b_2} \right) + 1 - \left( \frac{V_1 - b_1}{V_2 - b_2} \right) + \ln \gamma_i^{res,\infty} \quad (17)$$

We focus on the first bracketed term of equation (17) known as combinatorial-free volume term. The second contribution of equation (17) is the residual or energetic one. The combinatorial-free volume term includes all the non-energetic effects of a system/solution i.e. those arising from the differences in size and shape between the molecules. This is the most important term which should be adequately described by a thermodynamic model.

The similarity of the (functional form of the) combinatorial-free volume term of equation (17) to “polymer” models such as Flory-Huggins:

$$\ln \gamma_1^\infty = \ln \frac{V_1}{V_2} + 1 - \frac{V_1}{V_2} \quad (18)$$

or Entropic - FV (Kontogeorgis et al., 1993):

$$\ln \gamma_1^\infty = \ln \left( \frac{V_1 - V_{w1}}{V_2 - V_{w2}} \right) + 1 - \left( \frac{V_1 - V_{w1}}{V_2 - V_{w2}} \right) \quad (19)$$

proves that the repulsive term of cubic EoS ( $\frac{RI}{V-b}$ ) may be suitable for asymmetric systems even polymers unlike contrary to the common so far beliefs.

## Conclusions

The description of phase equilibria which is the key quantity in applied thermodynamics for the design of separation equipment e.g. distillation columns is performed with thermodynamic models. These are usually the cubic equations of state and the activity coefficient models. Inherent in these models are the mixing and combining rules employed which highly affect the performance of the models. In this work we have presented the interrelations between the various thermodynamic functions which provide with useful information on the range of the applicability of the equations of state. Despite the fact that such interrelations are known in the literature, their application including their limiting behavior at zero pressure, infinite pressure and zero concentration range for establishing the applicability limits of the models have received limited attention in the literature and this only in the recent years (Kontogeorgis and Vlamos, 1998; Kontogeorgis et al., 1998).

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