Relationships of McMillan-Mayer and Lewis-Randall Framework

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Introduction

- The need for a thermodynamic framework for prediction and correlation of phase equilibria
    - Dilute systems containing electrolytes, polymers and biomolecules

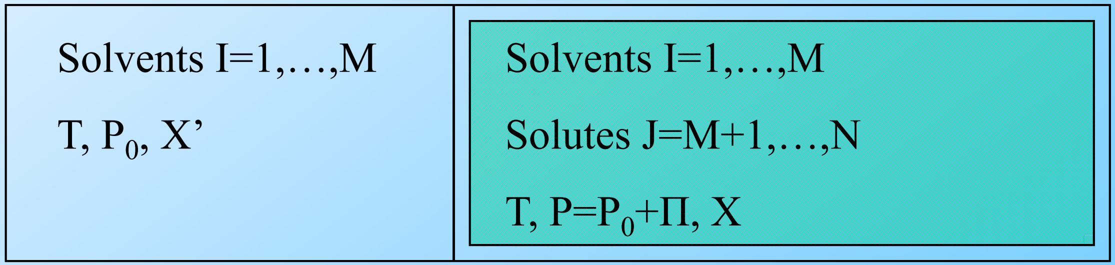
- The need for simultaneous models describing various phase equiliria
    - Hydrate equilibria containing alcohols, salts, etc.
    - High pressure equilibria containing eletrolytes

- Thermodynamic inconsistency between thermodynamic models
    - MSA, Debye-Hückel, etc. : McMillan-Mayer frameworks
    - UNIQUAC, NRTL, SAFT etc. : Lewis-Randall frameworks

Comparisons of McMillan-Mayer and Lewis-Randall

- McMillan-Mayer
  - The solvent molecules are replaced by a dielectric continuum.
  - An osmotic experiment where the solvent chemical potentials are kept constant.
  - Neglecting the effect of solvent-solvent and solvent-solute interactions.
  - Independent variables : temperature, pressure

    chemical potentials of solvents and numer of moles of solutes



Solvents I=1,…,M

T, P_0, X'

Solvents I=1,…,M

Solutes J=M+1,…,N

T, $P=P_0+\Pi$, X

Comparisons of McMillan-Mayer and Lewis-Randall

- Lewis-Randall(MR) Framework
  - An analysis under constant temperature and constant pressure
  - Independent variables : temperature, pressure

    number of moles of solutes

Solvents and Solutes

T, P, X

Comparisons of McMillan-Mayer and Lewis-Randall

- Isothermal Gibbs-Dühem equation
  - Lewis-Randall

$$VdP = \sum_{i=solvents} N_i d\ln\gamma_i + \sum_{j=solutes} N_j d\ln\gamma_j$$

  - McMillan-Mayer

$$VdP = \sum_{j=solutes} N_j d\ln\gamma_j$$

- It is impossible to obtain the expression for the chemical potentials of solvents in the McMillan-Mayer frameworks.

Conversion of MM to MR (Haynes et al., 1998)

- Legendre Transformation from Q to Ξ
  - Changes of independent variables from T, V, moles numbers to T,V, and chemical potentials
  - $$\Xi(\mu_0,\mu_1,T,V)=\sum_{N_0}\sum_{N_1}\exp\left(\frac{N_0\mu_0+N_1\mu_1}{N_{Av}kT}\right)Q(N_0,N_1,T,V) \qquad (1)$$
  - $$A=-kT\ln Q \text{ and } PV=kT\ln\Xi \qquad (2)$$
  - By comparison of equation (1) and (2)

$$-PV=A-n_0\mu_0-n_1\mu_1 \qquad (3)$$

Conversion of MM to MR (Haynes et al., 1998)

- Transformations of mole numbers to chemical potentials of solvent as independent variables by Legendre transformation
- $A'\left(T, V, \mu_0, n_j (j \neq solvent)\right) = A\left(T, V, n_i (i = all\ species)\right) - n_0 \mu_0$

  (4)
- In equation (4), A' is the natural thermodynamic potential working in the McMillan-Mayer framework.
- Excess Pressure
  - ◆ Solvent contribution such as hydration or ordering effects
  - ◆ $RT \ln \gamma_i (LR) = \mu'_{i,EX} (MM) - \overline{V}_i P_{EX} (Long - range)$

Conversion of Experimental Data (Lee, 2000)

- Osmotic coefficients

$$\ln a_w = -\phi^{LR} \frac{\sum_i m_i}{1000/M_w} = -\frac{P_{osm}\left\langle \overline{V}_w \right\rangle}{kT} = -\phi^{MM} \rho \left\langle \overline{V}_w \right\rangle$$

- Activity coefficients

$$RT \ln \gamma_i^{MM} - RT \ln \gamma_i^{LR} = \beta P_{osm} < \overline{V}_i >= \phi^{MM} \rho < \overline{V}_i >$$

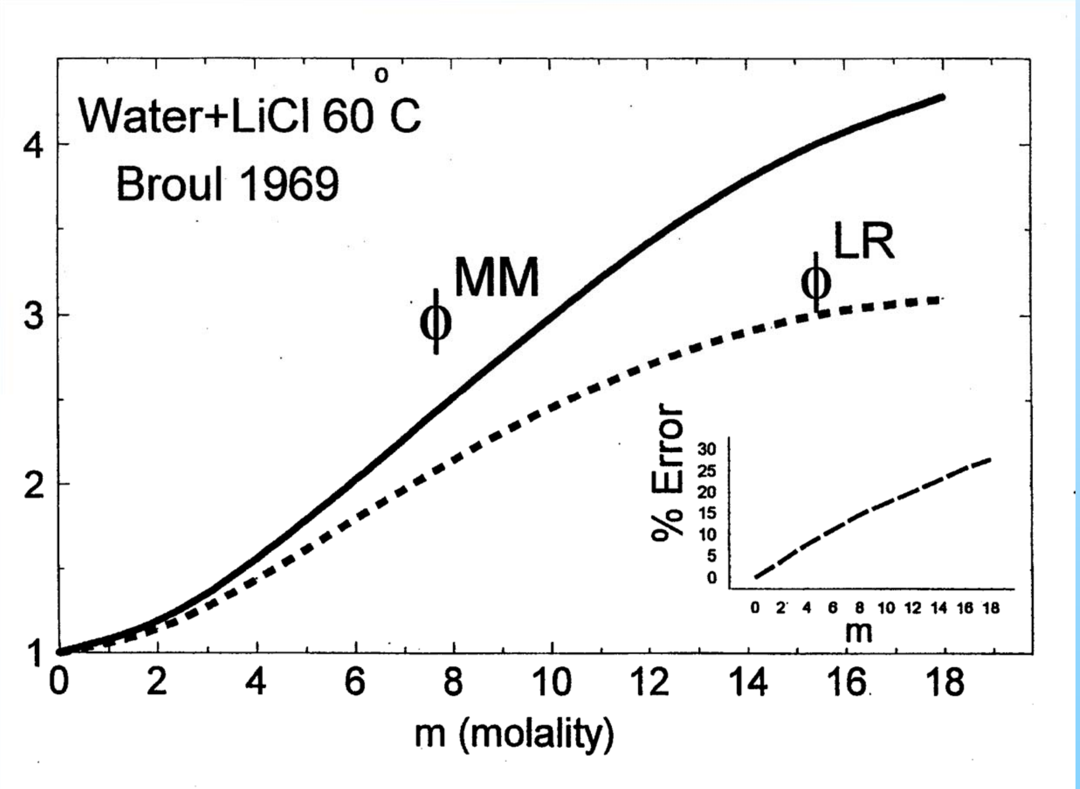


Figure 1.Osmotic coefficients MM and LR for water+LiCl system at 60°C

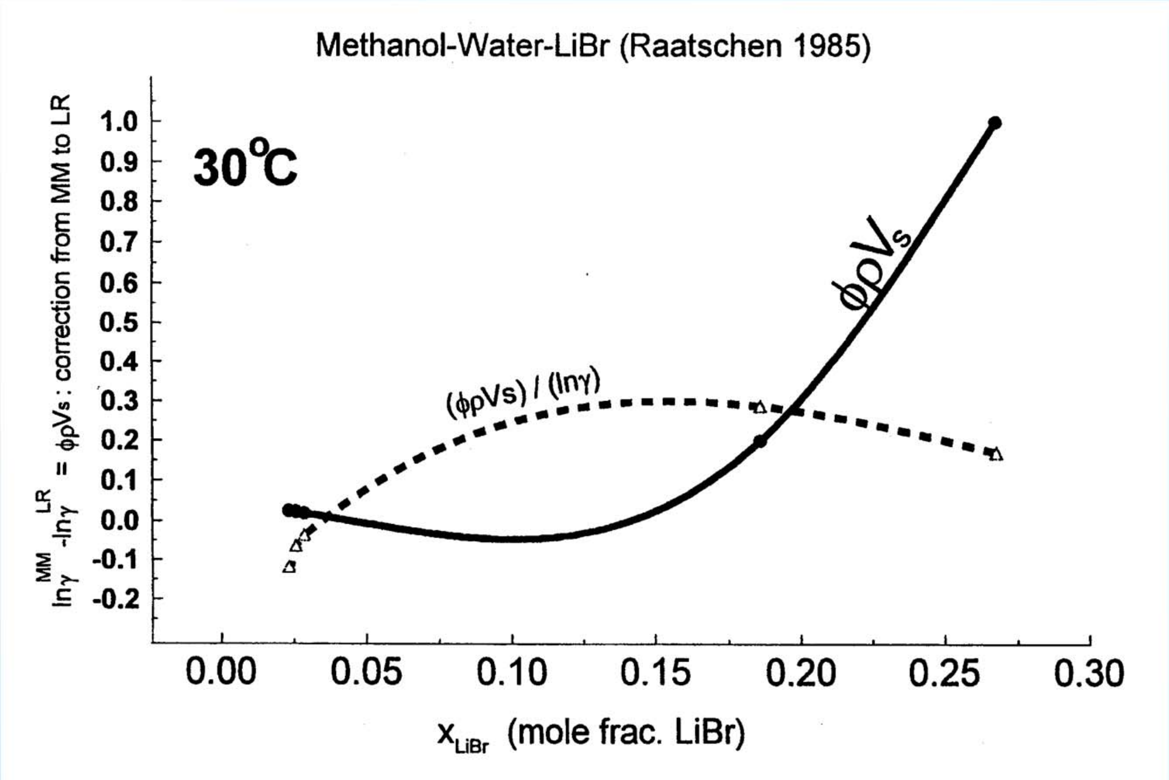


Figure 2. Correction (solid line) and ratio to total $\ln\gamma^{LR}$ (dashes)

Conclusion

- The comparison of MM and LR framework was accomplished
- The conversion of MM to LR framework was carried on by Legendre transformation.
- The deviations between MM and LR framework were investigated using the experimental data.

References

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