Thermodynamics of pure substances II

Overview of Lecture

- Residual properties and residual property functions.
- Departure functions.

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Residual properties

- A property defined relative to its ideal gas value at the same temperature and pressure is termed a ***residual property***

$$m^R(T,p) = m(T,p) - m^{ig}(T,p)$$

- For example – residual volume is

$$v^R(T,p) = v - v^{ig} = v - \frac{RT}{p}$$

- Usual property definitions also apply for residual properties; *e.g.*

$$g^R(T,p) = h^R - Ts^R$$

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Use of residual properties

- By definition

problem

$$g_2 - g_1 = (h_2 - h_1) - (T_2 s_2 - T_1 s_1)$$

- However, we may show that

$$h(p,T) = h_0^{ig}(p_0,T_0) + \int_{T_0}^{T} C_p^{ig}\,dT + h^R(T,p)$$

$$s(p,T) = s_0^{ig}(p_0,T_0) + \int_{T_0}^{T} \frac{C_p^{ig}}{T}\,dT - R\ln\left(\frac{p}{p_0}\right) + s^R(p,T)$$

which can then be used to evaluate g provided we can get our hands on the residual enthalpy and entropy.

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Determination of residual properties I

- It may be show that

$$d\left(\frac{g^R}{RT}\right) = \frac{v^R}{RT}\,dp - \frac{h^R}{RT^2}\,dT$$

and therefore

$$\frac{v^R}{RT} = \left.\frac{\partial\left(g^R/RT\right)}{\partial p}\right|_T \quad \text{and} \quad \frac{h^R}{RT} = -T\left.\frac{\partial\left(g^R/RT\right)}{\partial T}\right|_p$$

- Similarly

$$\frac{p^R}{RT} = -\left.\frac{\partial\left(a^R/RT\right)}{\partial p}\right|_T \quad \text{and} \quad \frac{u^R}{RT} = -T\left.\frac{\partial\left(a^R/RT\right)}{\partial T}\right|_p$$

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Determination of residual properties II

- Example 6.1

  Derive expressions for g^R, v^R, h^R and s^R for a gas described by the virial equation of state.

- Example 6.2

  Simplify the equations from example 6.1 for the case of the Virial expansion up to two-body terms.

- Example 6.3

  Derive expressions for g^R, v^R, h^R and s^R for a gas described by the van der Waals equation of state.

- Expressions such as those derived in the above examples are termed ***residual property functions*** or ***departure functions***.

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Wrap-up

- A residual properties is a property expressed relative to its ideal gas value at the same temperature and pressure.
- We may derive expressions for thermodynamic properties at a given pT or vT using the residual property concept.
- Expressions for residual properties may be derived from EOS.
- These expressions are termed residual property functions or departure functions.