

## Thermodynamic Properties of Real Gases

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### OBJECTIVES

- To define the Gibbs and Helmholtz energies (pp 199-201)
- Introduce the Maxwell Equations (p 201)
- Use the Maxwell equations to develop enthalpy and entropy relationships (pp. 202-208)
- Introduce residual properties (pp. 208-211)
- Use residual properties to develop expressions of H and S for real gases (pp. 212-220)

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## GIBBS AND HELMHOLTZ ENERGIES

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Consider material equilibrium in a system (closed, with constant mass) held at constant T and P, capable only of P-V work :

$$G \equiv H - TS$$

Consider material equilibrium in a system held at constant T and V, capable only of P-V work :

$$A \equiv U - TS$$

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## Fundamental Property Relationships

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For closed systems with changes occurring between equilibrium states :

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$

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## Maxwell's Equations

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These equations form the basis of other equations relating thermodynamic properties

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

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## Use of Maxwell Equations

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### Enthalpy relations

- homogeneous fluid of constant composition

$$dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

- liquids

$$dH = C_p dT + [V(1 - \beta T)] dP$$

- ideal gases

$$dH^{ig} = C_p^{ig} dT$$

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### Entropy Relationships

- homogeneous fluid of constant composition

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

- liquids

$$dS = \frac{C_p}{T} dT - \beta V dP$$

- ideal gases

$$dS^{ig} = \frac{C_p^{ig}}{T} dT - \frac{R}{P} dP$$

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## EXAMPLE

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Compute the change in enthalpy and entropy for water being pumped from an initial pressure of 101.3 kPa and 20°C to 3000 kPa and 60°C. The volume expansivity of water is  $6.48 (10^{-4})\text{K}^{-1}$  at 60 °C and 3000 kPa and the heat capacity of water is 75.3 J/(mol K).

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## EXAMPLE

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Estimate the change in temperature of liquid water initially at 25 °C being compressed from 1 atm to 200 atm.

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## Thermodynamic Properties of Fluids

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Real gases

- we want to know H, S as a function of T and P
- recall Gibbs free energy

$$dG = VdP - SdT$$

- from this we can derive

$$\frac{H}{RT} = -T \left[ \frac{\partial \left( \frac{G}{RT} \right)}{\partial T} \right]_P \quad \frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

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## Residual Properties

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departure from ideal behavior

$$G^R = G - G^{ig}$$

$G^R$  = residual Gibbs free energy

- note that residual properties can be written for other thermodynamic properties (V, H, S)

$$\frac{H^R}{RT} = -T \left[ \frac{\partial \left( \frac{G^R}{RT} \right)}{\partial T} \right]_P \quad \frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

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## How do you find $G^R$ ?

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recall for non-ideal gases (e.g., real gases)

$$PV = ZRT$$

from which we can derive

$$\frac{G^R}{RT} = \int_0^P \frac{(Z-1)}{P} dP \quad \frac{H^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P \frac{(Z-1)}{P} dP$$

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## Calculating H and S

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finally,

$$H = H_o^{ig} + \int_{T_o}^T C_p^{ig} dT + H^R$$

$$S = S_o^{ig} + \int_{T_o}^T \frac{C_p^{ig}}{T} dT - R \ln \left( \frac{P}{P_o} \right) + S^R$$

where  $T_o$  and  $P_o$  are ideal gas reference conditions

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## Real Gases : Residual Properties

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Redlich-Kwong Equation :

$$\frac{H^R}{RT} = Z - 1 - \frac{7.4}{T_r^{1.5}} \ln \left( 1 + \frac{0.08664P_r}{ZT_r} \right)$$

$$\frac{S^R}{R} = \ln \left( Z - \frac{0.08664P_r}{T_r} \right) - \frac{2.467}{T_r^{1.5}} \ln \left( 1 + \frac{0.08664P_r}{ZT_r} \right)$$

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## Real Gases : Residual Properties

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Generalized Virial Correlations for Gases :

$$\frac{H^R}{RT_c} = P_r \left[ B^0 - \frac{0.675}{T_r^{1.6}} + \omega \left( B^1 - \frac{0.722}{T_r^{4.2}} \right) \right]$$

$$\frac{S^R}{R} = -P_r \left[ \frac{0.675}{T_r^{2.6}} + \omega \left( \frac{0.722}{T_r^{5.2}} \right) \right]$$

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## EXAMPLE

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n-butane is compressed from 1 atm and 25 °C to 25 atm and 510 K. Calculate the change in enthalpy and change in entropy for this process.