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Lecture Notes 6

E134 – 2023-09-14

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Chapter 6 Fundamental Property Relationships

One phase homogeneous systems – 2 degrees of freedom

U	$dU = TdS - PdV$
$H \equiv U + PV$	$dH = TdS + VdP$
$A \equiv U - TS$	$dA = -PdV - SdT$
$G \equiv H - TS$	$dG = VdP - SdT$

Note that the xdy terms all have an intrinsically intensive variable, P or T, and a potentially extensive variable, $S^t = nS$ or $U^t = nV$.

Which is most useful experimentally?

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After a lot of simple calculus

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

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

What is the utility?

We can calculate H and S as functions of T and P, which are variables we can control.

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From the above relationships and the ideal gas law,

$$V = \frac{RT}{P},$$

do we recover the known relationships for H and S for an ideal gas?

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To evaluate we need $C_P(T)$ and

$$V(T,P) \text{ or } \beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Then

$$dH = C_P dT + V[1 - \beta T]dP$$

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

For a single-phase homogeneous system we can get all thermodynamic properties from C_P data and β data.

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From the text

$$dH = C_P\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \quad (6.21)$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \quad (6.22)$$

See pages 217-218 for the derivations of U and S as functions of T and V.

$$dU = C_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \quad (6.32)$$

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \quad (6.33)$$

Residual Properties

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For a generic thermodynamic property, M, we define the *residual M* as

$$M^R \equiv M - M^{ig}$$

For example

$$V^R = V - V^{ig} = \frac{ZRT}{P} - \frac{RT}{P} = \frac{RT}{P}(Z-1)$$

Why is M^R useful?

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$$dG = VdP - SdT$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT$$

For an isotherm (T = const).

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP$$

$$\frac{G^R}{RT} = \int_0^P \frac{V^R}{RT}dP = \int_0^P (Z-1)\frac{dP}{P} = \frac{H^R}{RT} - T\frac{S^R}{RT} \quad \text{(at constant } T\text{)}$$

We can get Z or $Z-1$ from an equation of state or from the generalized correlations.

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For residual enthalpy, $\frac{H^R}{RT}$, and entropy, $\frac{S^R}{R}$.

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega\frac{(H^R)^1}{RT_c} \quad (6.66)$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega\frac{(S^R)^1}{R} \quad (6.67)$$

In Tables D.5 through D.12.

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For when the linear approximation holds ($Z \geq 0.8$, $P_r \leq 2$).

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$$\frac{H^R}{RT_c} = P_r \left[B^0 - T_r \frac{dB^0}{dT_r} + \omega \left(B^1 - T_r \frac{dB^1}{dT_r} \right) \right] \quad (6.68)$$

$$\frac{S^R}{R} = -P_r \left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right) \quad (6.69)$$

where

$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$ (3.61)	$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$ (3.62)
$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}}$ (6.70)	$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$ (6.71)

Example 6.5

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Calculate ΔH and ΔS for CO_2 at 70°C and 150 bar (State 1) going to 20°C and 15 bar (State 2)

$$\Delta H = H_2^R + \Delta H_{1-2}^{ig} - H_1^R$$

$$\Delta S = S_2^R + \Delta S_{1-2}^{ig} - S_1^R$$

$$T_c = 304.2 \text{ K}, \; P_c = 73.83 \text{ bar}, \; \omega = 0.224$$

$$T_{r_1} = \frac{70 + 273.15}{304.2} = 1.128 \; , \; P_{r_1} = \frac{150}{73.83} = 2.032$$

$$T_{r_2} = \frac{20 + 273.15}{304.2} = 0.964 \; , \; P_{r_2} = \frac{15}{73.83} = 0.203$$

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To interpolate, remember that the slopes are the same

$$\frac{y - y_2}{x - x_2} = \frac{y_1 - y_2}{x_1 - x_2} \Rightarrow y = y_2 + \frac{y_1 - y_2}{x_1 - x_2}(x - x_2)$$

Doubly interpolating in Tables D.5 through D.12.

At State 1

$$\frac{\left(H^R\right)^0}{RT_c} = -2.709\ , \quad \frac{\left(H^R\right)^1}{RT_c} = -0.921$$

$$\frac{\left(S^R\right)^0}{RT_c} = -1.846\ , \quad \frac{\left(S^R\right)^1}{RT_c} = -0.938$$

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At State 2

$$\frac{\left(H^R\right)^0}{RT_c} = -0.234\ , \quad \frac{\left(H^R\right)^1}{RT_c} = -0.233$$

$$\frac{\left(S^R\right)^0}{RT_c} = -0.165\ , \quad \frac{\left(S^R\right)^1}{RT_c} = -0.220$$

$$H_1^R = RT_c(-2.709 + 0.224 \cdot -0.921) = -7373 \text{ J/mol}$$

$$S_1^R = R(-1.846 + 0.224 \cdot -0.938) = -17.10 \text{ J/mol K}$$

$$H_2^R = RT_c(-0.234 + 0.224 \cdot -0.233) = -723 \text{ J/mol}$$

$$S_2^R = R(-0.165 + 0.224 \cdot -0.220) = -2.23 \text{ J/mol K}$$

$$\Delta H^{ig}_{1-2} = R\left[A\left(T_2 - T_1\right) + \frac{B}{2}\left(T_2^2 - T_1^2\right) + D\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

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$A = 5.457$ (in example book uses 5.547)

$B = 1.045 \times 10^{-3}$

$D = -1.157 \times 10^{5}$

$\Delta H^{ig}_{1-2} = -1929$ J/mol

$\Delta H = \Delta H^{ig}_{1-2} + H^R_2 - H^R_1 =$ **4721 J/mol**

$$\Delta S^{ig}_{1-2} = R\left[A\ln\frac{T_2}{T_1} + B\left(T_2 - T_1\right) + \frac{D}{2}\left(\frac{1}{T_1^2} - \frac{1}{T_2^2}\right)\right] - R\ln\frac{P_2}{P_1}$$

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$\Delta S^{ig}_{1-2} = 13.08$ J/mol K

$\Delta S = \Delta S^{ig}_{1-2} + S^R_2 - S^R_1 =$ **27.95 J/mol K**

Alternate, using Generalized Correlations with 2nd Virial Coefficient

$$B^0 = -0.3647\ ,\ \ B^1 = -0.0619$$

$$\frac{dB^0}{dT_r} = 0.7432\ ,\ \ \frac{dB^1}{dT_r} = 0.8752$$

$$H_2^R = -660 \text{ J/mol}\ ,\ \ S_2^R = -1.59 \text{ J/mol K}$$

$$\Delta H = \Delta H_{1-2}^{ig} + H_2^R - H_1^R = \mathbf{4785\ J/mol}$$

$$\Delta S = \Delta S_{1-2}^{ig} + S_2^R - S_1^R = \mathbf{28.59\ J/mol\ K}$$