

Problem Set 10 - Solutions

Problem 6.1

- (a) Starting with the definition of the Helmholtz energy in Equation 6.3, derive the fundamental property relation in Equation 6.10
- (b) Starting with the definition of the Gibbs energy in Equation 6.4, derive the fundamental property relation in Equation 6.11.

Solution

Reference - screenshot from lesson 27 slide 6:

Additional properties arise by definition:

$$\text{Enthalpy: } H \equiv U + PV \quad (\text{Eq. 6.2})$$

$$\text{Helmholtz Energy: } A \equiv U - TS \quad (\text{Eq. 6.3})$$

$$\text{Gibbs Energy: } G \equiv H - TS \quad (\text{Eq. 6.4})$$

Reference - screenshot from lesson 27 slide 8:

General equations for a homogenous fluid of constant composition.

$dU = TdS - PdV$ ✓ (Eq. 6.8)	$dH = TdS + VdP$ ✓ (Eq. 6.9)
$dA = -PdV - SdT$? (Eq. 6.10)	$dG = VdP - SdT$? (Eq. 6.11)

Part (a)

Introduce the definition of Helmholtz energy, equation 6.3:

Out[=]//TraditionalForm=

$$A \equiv U - ST$$

Take the total differential of A:

Out[=]//TraditionalForm=

$$dA = dU - TdS - SdT$$

Fundamental property relation for U, Equation 6.8, presented in class:

Out[=]//TraditionalForm=

$$dU = TdS - PdV$$

Substitute equation 6.8 into the equation for dA :

Out[=]//TraditionalForm=

$$dA = TdS - PdV - TdS - SdT$$

Simplify by cancelling $T dS$, giving equation 6.10:

Out[=]//TraditionalForm=

$$dA = -PdV - SdT$$

Part (b)

Introduce the definition of Gibbs energy, equation 6.4:

Out[=]//TraditionalForm=

$$G \equiv H - ST$$

Take the total differential of G :

Out[=]//TraditionalForm=

$$dG = dH - SdT - TdS$$

Fundamental property relation for H , Equation 6.9, presented in class:

Out[=]//TraditionalForm=

$$dH = TdS + VdP$$

Substitute equation 6.9 into the equation for dG :

Out[=]//TraditionalForm=

$$dG = TdS + VdP - SdT - TdS$$

Simplify by cancelling $T dS$, giving equation 6.11:

Out[=]//TraditionalForm=

$$dG = VdP - SdT$$

Problem 6.4

(a) Starting with the fundamental property relation Equation 6.10, derive the Maxwell relation given in Equation 6.16.

(b) Starting with the fundamental property relation Equation 6.9, derive the Maxwell relation given in Equation 6.15.

Solution

Reference - screenshot from lesson 27 slide 8:

General equations for a homogenous fluid of constant composition.

$dU = TdS - PdV \quad \checkmark$ (Eq. 6.8)	$dH = TdS + VdP \quad \checkmark$ (Eq. 6.9)
$dA = -PdV - SdT \quad ?$ (Eq. 6.10)	$dG = VdP - SdT \quad ?$ (Eq. 6.11)

Reference - screenshot from lesson 27 slide 12:

$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \quad \checkmark$ (Eq. 6.14)	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad ?$ (Eq. 6.15)
$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad ?$ (Eq. 6.16)	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad \checkmark$ (Eq. 6.17)

Part (a)

Introduce the fundamental property relationship equation 6.10:

$$dA = -PdV - SdT$$

Introduce the function $A = A(V, T)$, where V and T are the canonical (special) variables, and take the total differential of A :

$$A = A(V, T)$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

Compare this result to equation 6.10 and equate the coefficients of the differentials:

$$P \equiv \left(\frac{\partial A}{\partial V}\right)_T$$

$$S \equiv \left(\frac{\partial A}{\partial T}\right)_V$$

Take the second partial cross-derivatives and equate them:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \left(-\left(\frac{\partial A}{\partial V}\right)_T\right)\right)_V = -\frac{\partial^2 A}{\partial T \partial V}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial}{\partial V} \left(-\left(\frac{\partial A}{\partial T}\right)_V\right)\right)_T = -\frac{\partial^2 A}{\partial V \partial T}$$

$$-\frac{\partial^2 A}{\partial T \partial V} = -\frac{\partial^2 A}{\partial V \partial T}$$

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

This is the Maxwell relationship equation 6.16. //ANS

Part (b)

Introduce the fundamental property relationship equation 6.9:

$$dH = T dS + V dP$$

Introduce the function $H = H(S, P)$, where S and P are the canonical (special) variables, and take the total differential of H :

$$H = H(S, P)$$

$$dH = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dP$$

Compare this result to equation 6.9 and equate the coefficients of the differentials:

$$T \equiv \left(\frac{\partial H}{\partial S} \right)_P$$

$$V \equiv \left(\frac{\partial H}{\partial P} \right)_S$$

Take the second partial cross-derivatives and equate them:

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial}{\partial P} \left(\left(\frac{\partial H}{\partial S} \right)_P \right) \right)_S = \frac{\partial^2 H}{\partial P \partial S}$$

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial}{\partial S} \left(\left(\frac{\partial H}{\partial P} \right)_S \right) \right)_P = \frac{\partial^2 H}{\partial S \partial P}$$

$$\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P}$$

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

This is the Maxwell relationship equation 6.15. //ANS

Problem 6.141

Calculate Z, H^R , and S^R by the Redlich-Kwong equation for the following:

- (a) Ethylene at 300 K and 35 bar.
- (b) Hydrogen sulfide at 400 K and 70 bar.
- (c) Nitrogen at 150 K and 50 bar.
- (d) n-Octane at 575 K and 15 bar.
- (e) Propane at 375 K and 25 bar.

Solution

Part (a) - Ethylene at 300 K and 35 bar

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In[1]:= (*Temperature and Pressure*)
t = 300.; (*K*)
p = 35.; (*bar*)

(*Ethylene Properties from Table B.1, p.664*)
tc = 282.3; (*K*)
pc = 50.40; (*bar*)
ω = 0.087; (*not used in RK EOS*)

(*Reduced T and P*)
tr = t / tc; (*reduced temperature*)
pr = p / pc; (*reduced pressure*)

(*Equation of state supporting information from Table 3.1 page 100*)
σ = 1;
ε = 0;
Ω = 0.08664;
Ψ = 0.42748;
α[x_] = x-1/2; (*Table 3.1*)

(*Equation of state*)
β = Ω * pr / tr; (*eq 3.50*)
q[x_] = (Ψ * α[x]) / (Ω * x); (*eq 3.50*)
eq1 = z = 
$$\left( 1 + \beta - q[tr] * \beta * \frac{z - \beta}{(z + \epsilon * \beta) * (z + \sigma * \beta)} \right); (*Eq. 3.48*)$$


(*Solve for Z*)
Z = z /. Solve[eq1, z, Reals][[1, 1]] // Quiet(*//ANS*)

(*Solve for the Integral*)
Integral = 
$$\frac{1}{\sigma - \epsilon} * \text{Log}\left[\frac{z + \sigma * \beta}{z + \epsilon * \beta}\right]; (*Eq. 13.72*)$$


(*Solve for Residuals HR and SR)
R = 8.314; (*J/mol*K*)
Hr[x_] = (Z - 1 + x * ∂x q[x] * Integral) * R * t; (*L28 Slide 8*)
Sr[x_] = (Log[Z - β] + (q[x] + x * ∂x q[x]) * Integral) * R;

Hr[tr]
Sr[tr]

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Out[]=
0.771 2007

Out[]=
-1 764.407

Out[]=
-4.120 333

$$Z = 0.7712 \text{ //ANS; } H^R = -1764.407 \frac{J}{\text{mol}} \text{ //ANS; } S^R = -4.12033 \frac{J}{\text{mol}\cdot K} \text{ //ANS}$$

Part (b) - Hydrogen sulfide at 400 K and 70 bar

Part (c) - Nitrogen at 150 K and 50 bar

Part (d) - n-Octane at 575 K and 15 bar

Part (e) - Propane at 375 K and 25 bar

Solution Grid

Z	H ^R $\frac{J}{\text{mol}}$	S ^R $\frac{J}{\text{mol}\cdot K}$
(a) 0.7712	-1,764.407	-4.120
(b) 0.7445	-2,658.792	-4.698
(c) 0.6629	-1,488.048	-7.257
(d) 0.7658	-3,389.758	-4.115
(e) 0.7750	-2,121.920	-3.939