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 to Part (a)

Introduce the definition of Helmholtz energy, equation 6.3:

Out[∘]//TraditionalForm=

$$A \equiv U - S\,T$$

Take the total differential of A:

Out[∘]//TraditionalForm=

$$\mathrm{dA} = \mathrm{dU} - \mathrm{Td}\,S - \mathrm{SdT}$$

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

Out[∘]//TraditionalForm=

$$\mathrm{dU} = \mathrm{TdS} - \mathrm{PdV}$$

Substitute equation 6.8 into the equation for dA:

Out[∘]//TraditionalForm=

$$\mathrm{dA} = \mathrm{TdS} - \mathrm{PdV} - \mathrm{Td}\,S - \mathrm{SdT}$$

Simplify by cancelling T dS, giving equation 6.10:

Out[∘]//TraditionalForm=

$$\mathrm{dA} = -\mathrm{PdV} - \mathrm{SdT}$$

Solution to Part (b)

Introduce the definition of Gibbs energy, equation 6.4:

Out[∘]//TraditionalForm=

$$G \equiv H - S\,T$$

Take the total differential of G:

Out[∘]//TraditionalForm=

$$\mathrm{dG} = \mathrm{dH} - \mathrm{SdT} - \mathrm{TdS}$$

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 to Part (a)

Introduce the fundamental property relationship equation 6.10:

$$d A = -P d V - S d T$$

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

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

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

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

Solution to Part (b)

Introduce the fundamental property relationship equation 6.9:

$$d H = T\, d S + V\, d P$$

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

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

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

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

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

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

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 to Part (a)

```
p = 35.; (*bar*)
pc = 50.40; (*bar*) (*Table B.1, p.664*)
pr = p / pc; (*reduced pressure*)
```

In[121]:=

```
t = 300.; (*K*)
tc = 282.3; (*K*) (*Table B.1, p.664*)
tr = t / tc; (*reduced temperature*)
```

In[124]:=

```
(*Information from Table 3.1 page 100*)
ϵ = 0;
σ = 1;
Ω = 0.08664;
Ψ = 0.42748;
(*ω=.087  Table B.1 p.664 but not needed for RK EOS*)
```

In[128]:=

```
α[x_] = x^(-1/2); (*Table 3.1*)
β = Ω * pr / tr; (*eqs 3.50 and 3.51*)
q[x_] = (Ψ * α[x]) / (Ω * x);
```

In[131]:=

$$eq1 = z == \left(1 + \beta - q[tr] * \beta * \frac{z - \beta}{(z + \epsilon * \beta) * (z + \sigma * \beta)}\right); (*Eq.\ 3.48*)$$

In[132]:=

```
Z = z /. Solve[eq1, z, Reals][[1, 1]] // Quiet
```

Out[132]=

```
0.771200680752
```

In[133]:=

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

In[134]:=

$R = 8.314; (*\frac{J}{mol*K}*)$

$Hr[x\_] = (Z - 1 + x * \partial_x q[x] * Integral) * R * t;$ (*L28 Slide 8*)

$Sr[x\_] = (Log[Z - \beta] + (q[x] + x * \partial_x q[x]) * Integral) * R;$

In[137]:=

```
Hr[tr]
Sr[tr]
```

Out[137]=

```
-1764.40667518
```

Out[138]=

```
-4.12033343009
```

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

Solution to Part (b)

In[155]:=

```
p = 70.; (*bar*)
pc = 89.63; (*bar*) (*Table B.1, p.665*)
pr = p / pc; (*reduced pressure*)
```

In[158]:=

```
t = 400.; (*K*)
tc = 373.5; (*K*) (*Table B.1, p.665*)
tr = t / tc; (*reduced temperature*)
```

In[161]:=

```
α[x_] = x^(-1/2); (*Table 3.1*)
β = Ω * pr / tr; (*eqs 3.50 and 3.51*)
q[x_] = (Ψ * α[x]) / (Ω * x);
```

In[164]:=

$$\text{eq1} = z == \left(1 + \beta - q[tr] * \beta * \frac{z - \beta}{(z + \epsilon * \beta) * (z + \sigma * \beta)}\right); \text{(*Eq. 3.48*)}$$

In[165]:=

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

Out[165]=

```
0.744472607587
```

In[166]:=

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

In[167]:=

$$R = 8.314; \left(*\frac{J}{mol*K}*\right)$$

$$\text{Hr}[x\_] = (Z - 1 + x * \partial_x q[x] * \text{Integral}) * R * t; \text{(*L28 Slide 8*)}$$

$$\text{Sr}[x\_] = (\text{Log}[Z - \beta] + (q[x] + x * \partial_x q[x]) * \text{Integral}) * R;$$

In[170]:=

```
Hr[tr]
Sr[tr]
```

Out[170]=

```
-2658.79192074
```

Out[171]=

```
-4.69814218997
```

$Z = 0.7445$ //ANS; $H^R = -2658.792\ \frac{J}{mol}$ //ANS; $S^R = -4.698\ \frac{J}{mol\,K}$ //ANS

Solution to Part (c)

In[172]:=

```
p = 50.; (*bar*)
pc = 34.00; (*bar*) (*Table B.1, p.665*)
pr = p / pc; (*reduced pressure*)
```

In[175]:=

```
t = 150.; (*K*)
tc = 126.2; (*K*) (*Table B.1, p.665*)
tr = t / tc; (*reduced temperature*)
```

In[178]:=

```
α[x_] = x^(-1/2);  (*Table 3.1*)
β = Ω * pr / tr; (*eqs 3.50 and 3.51*)
q[x_] = (Ψ * α[x]) / (Ω * x);
```

In[181]:=

$$eq1 = z == \left(1 + \beta - q[tr] * \beta * \frac{z - \beta}{(z + \epsilon * \beta) * (z + \sigma * \beta)}\right); (*Eq.\ 3.48*)$$

In[182]:=

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

Out[182]=

```
0.662889058847
```

In[183]:=

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

In[184]:=

$R = 8.314; (*\frac{J}{mol*K}*)$

$Hr[x\_] = (Z - 1 + x * \partial_x q[x] * Integral) * R * t;\ (*L28\ Slide\ 8*)$

$Sr[x\_] = (Log[Z - \beta] + (q[x] + x * \partial_x q[x]) * Integral) * R;$

In[187]:=

```
Hr[tr]
Sr[tr]
```

Out[187]=

```
-1488.04767962
```

Out[188]=

```
-7.25732313512
```

$Z = 0.6629$ //ANS; $H^R = -1488.048\ \frac{J}{mol}$ //ANS; $S^R = -7.257\ \frac{J}{mol\,K}$ //ANS

Solution to Part (d)

In[189]:=

```
p = 15.; (*bar*)
pc = 24.90; (*bar*) (*Table B.1, p.663*)
pr = p / pc; (*reduced pressure*)
```

In[192]:=
```
t = 575.; (*K*)
tc = 568.7; (*K*) (*Table B.1, p.663*)
tr = t / tc; (*reduced temperature*)
```

In[195]:=
```
α[x_] = x^(-1/2); (*Table 3.1*)
β = Ω * pr / tr; (*eqs 3.50 and 3.51*)
q[x_] = (Ψ * α[x]) / (Ω * x);
```

In[198]:=

$$eq1 = z == \left(1 + \beta - q[tr] * \beta * \frac{z - \beta}{(z + \epsilon * \beta) * (z + \sigma * \beta)}\right); (*Eq.\ 3.48*)$$

In[199]:=
```
Z = z /. Solve[eq1, z, Reals][[1, 1]] // Quiet(*//ANS*)
```

Out[199]=
```
0.765801774832
```

In[200]:=

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

In[201]:=

$$R = 8.314; \left(*\frac{J}{mol*K}*\right)$$
$$Hr[x\_] = (Z - 1 + x * \partial_x q[x] * Integral) * R * t;\ (*L28\ Slide\ 8*)$$
$$Sr[x\_] = (Log[Z - \beta] + (q[x] + x * \partial_x q[x]) * Integral) * R;$$

In[204]:=
```
Hr[tr]
Sr[tr]
```

Out[204]=
```
-3389.75788422
```

Out[205]=
```
-4.11468647157
```

$Z = 0.7658$ //ANS; $H^R = -3389.758\ \frac{J}{mol}$ //ANS; $S^R = -4.115\ \frac{J}{mol\,K}$ //ANS

Solution to Part (e)

In[206]:=
```
p = 25.; (*bar*)
pc = 42.48; (*bar*) (*Table B.1, p.663*)
pr = p / pc; (*reduced pressure*)
```

In[209]:=
```
t = 375.; (*K*)
tc = 369.8; (*K*) (*Table B.1, p.663*)
tr = t / tc; (*reduced temperature*)
```

In[212]:=
```
α[x_] = x^(-1/2); (*Table 3.1*)
β = Ω * pr / tr; (*eqs 3.50 and 3.51*)
q[x_] = (Ψ * α[x]) / (Ω * x);
```

In[215]:=

```
eq1 = z == (1 + β - q[tr] * β * (z - β)/((z + ϵ * β) * (z + σ * β))); (*Eq. 3.48*)
```

In[216]:=

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

Out[216]=

```
0.775001391061
```

In[217]:=

```
Integral = 1/(σ - ϵ) * Log[(Z + σ * β)/(Z + ϵ * β)]; (*Eq. 13.72*)
```

In[218]:=

```
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 ;
```

In[221]:=

```
Hr[tr]
Sr[tr]
```

Out[221]=

```
-2121.91582396
```

Out[222]=

```
-3.93946210323
```

$Z = 0.7750$ //ANS; $H^R = -2121.92\ \frac{J}{mol}$ //ANS; $S^R = -3.939\ \frac{J}{mol\,K}$ //ANS