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): Equation 6.10 is given in the problem statement, and we can use equation 6.1, which was presented in class:

$$dA = -PdV - SdT \tag{6.10}$$

$$d(nU) = Td(nS) - Pd(nV) \tag{6.1}$$

Introduce Helmholtz energy, $A \equiv U - TS$, Equation 6.3, and multiply by moles n:

$$A \equiv U - TS \tag{6.3}$$

$$nA = nU - TnS$$

Take the total differential of nA, substitute in d(nU), and simplify:

$$d(nA) = d(nU) - Td(nS) - (nS)dT$$

$$\begin{aligned} d(nA) &= Td(nS) - Pd(nV) - Td(nS) - (nS)dT \\ &= -Pd(nV) - (nS)dT \end{aligned} \tag{6.6}$$

For n=1 or for constant composition, this becomes:

$$dA = -PdV - SdT \tag{6.10}$$

Solution to Part (b): We can use equation 6.1, which was presented in class:

$$d(nU) = Td(nS) - Pd(nV) \tag{6.1}$$

Introduce Gibbs energy, $G \equiv H - TS$, Equation 6.4, and multiply by moles n:

$$G \equiv H - TS \tag{6.4}$$

$$nG = nH - TnS$$

Take the total differential of nG:

$$d(nG) = d(nH) - Td(nS) - (nS)dT$$

Use the fundamental relationship for enthalpy in the form of equation 6.5:

$$d(nH) = Td(nS) + (nV)dP \tag{6.5}$$

Substitute in d(nH) from Equation 6.5 and d(nU) from Equation 6.1, and simplify:

$$\begin{aligned}
d(nG) &= d(nH) - Td(nS) - (nS)dT \\
&= Td(nS) + (nV)dP - Td(nS) - (nS)dT \\
&= (nV)dP - (nS)dT
\end{aligned} \tag{6.7}$$

For n=1 or for constant composition, this becomes:

$$dG = VdP - SdT \tag{6.11}$$

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):

The starting point is the fundamental property relationship given by Equation 6.9:

$$dA = -PdV - SdT \qquad (6.9)$$

Then, introduce the function $A=A(V,T)$, where V and T are the *canonical* (special) variables. From there, take the total differential of A, equate P and S to the first partial derivatives, take the second partial cross-derivatives, and equate them. This will lead to the Maxwell relation Equation 6.16.

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

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

$$P \equiv -\left(\frac{\partial A}{\partial V}\right)_T \quad \text{and} \quad S \equiv -\left(\frac{\partial A}{\partial T}\right)_V$$

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

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

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

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad (6.16)$$

ANS

Solution to Part (b):

The starting point is the fundamental property relationship given by Equation 6.9:

$$dH = TdS + VdP \tag{6.8}$$

Introduce the function $H=H(S,P)$, where S and P are the *canonical* (special) variables. From there, take the total differential of H, equate T and V to the first partial derivatives, take the second partial cross-derivatives, and equate them. This will lead to the Maxwell relation Equation 6.15.

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

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

$$T \equiv \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V \equiv \left(\frac{\partial H}{\partial P}\right)_S$$

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

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

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

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{6.15}$$

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.

<u>Solution to Part (a), Ethylene at 300 K and 35 bar:</u>

```
Quit[];
```

In[ ]:=
```
p = 35.; (*bar*)
pc = 50.40; (*bar*) (*Table B.1, p.651*)
pr = p / pc; (*reduced pressure*)
```

In[ ]:=
```
t = 300.; (*K*)
tc = 282.3; (*K*) (*Table B.1, p.651*)
tr = t / tc; (*reduced temperature*)

(*Information from Table 3.1 page 100*)
ϵ = 0;
σ = 1;
Ω = 0.08664;
Ψ = 0.42748;
(*ω=.087  Table B.1 p.651 but not needed for RK EOS*)
```

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

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

Out[ ]=
```
0.771200680752
```

```
(*Z=0.7712 //ANS*)
```

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

In[ ]:=
```
R = 8.314; (* J/(mol*K) *)
Hr[x_] = (Z - 1 + x * ∂_x q[x] * Integral) * R * t; (*L28 Slide 7*)
Sr[x_] = (Log[Z - β] + (q[x] + x * ∂_x q[x]) * Integral) * R;
```

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

Out[●]=

-1764.40667518

Out[●]=

-4.12033343009

```
(*H^R=-1764.407 J/mol  //ANS*)
(*S^R=-4.120 J/mol*K  //ANS*)
```

Solution to (b) thru (e):

```
In[ ]:=  Quit[];

         (*Answers below are for Z, Hr in J/mol, and Sr in J/mol/K*)

         P = {70, 50, 15, 25};
         Pc = {89.63, 34.00, 24.90, 42.48};
         Pr = P / Pc;
         T = {400, 150, 575, 375};
         Tc = {373.5, 126.2, 568.7, 369.8};
         Tr = T / Tc;

         ϵ = 0;
         σ = 1;
         Ω = 0.08664;
         Ψ = 0.42748;
         α[x_] = x^(-1/2);
         β = Ω * Pr / Tr;
         q[x_] = (Ψ * α[x]) / (Ω * x);

         eq1 = Z - (1 + β - q[Tr] * β * ((Z - β) / ((Z + ϵ * β) * (Z + σ * β))));
         Zlist = Table[Z /. FindRoot[eq1[[i]], {Z, .9}], {i, 4}];
         Zlist // MatrixForm(*//ANS*)

         R = 8.314; (*J/(mol*K)*)
         Int = (1 / (σ - ϵ)) * Log[(Zlist + σ * β) / (Zlist + ϵ * β)];
         f[x_] = x * ∂x q[x];
         Hr = (Zlist - 1 + f[Tr] * Int) * R * T  // MatrixForm(*ANS, J/mol*)
         Sr = (Log[Zlist - β] + (q[Tr] + f[Tr]) * Int) * R // MatrixForm (*ANS, J/(mol*K)*)
```

Out[ ]//MatrixForm=
$$\begin{pmatrix} 0.744472607587 \\ 0.662889058847 \\ 0.765801774832 \\ 0.775001391061 \end{pmatrix}$$

Out[ ]//MatrixForm=
$$\begin{pmatrix} -2658.79192074 \\ -1488.04767962 \\ -3389.75788422 \\ -2121.91582396 \end{pmatrix}$$

Out[ ]//MatrixForm=
$$\begin{pmatrix} -4.69814218997 \\ -7.25732313512 \\ -4.11468647157 \\ -3.93946210323 \end{pmatrix}$$

```
         (*//ANS for Z, Hr in J/mol, and Sr in J/mol/K*)
```