

Example 4.3, page 128 of Smith, van Ness & Abbott

Preliminaries

```
> restart;
Convert initial temperature (500 F) to Kelvin, assign to Q the heat transferred per mol
> T0 := (500-32)/1.8 + 273.15;
   Q := 37218;
                                     T0 := 533.1500000
                                     Q := 37218
> R := 8.314; J/K-mol
                                     R := 8.314
```

Ideal-gas solution

```
Ideal-gas heat capacity of ammonia as a function of temperature, from Table C.1
> cp_ig := T -> R*(3.578 + 3.02e-3 * T - 0.186e5 / T^2);
                                     cp_ig := T -> R ( 3.578 + .00302 T - 18600. / T^2 )
Function for ideal-gas enthalpy change for change in temperature from T0 to T. Note that the T0
here is distinguished from the T0 set above, because it appears here as an argument to the
function.
> delH_ig := (T0,T) -> int(cp_ig(t),t=T0..T);
                                     delH_ig := (T0, T) -> ∫T0T cp_ig(t) dt
If we call the function with T0, T0 is now interpreted as the T0 defined above.
> delH_ig(T0,T);
                                     .00008314000000  $\frac{357800. T^2 + 151. T^3 + .18600000000 10^{10}}{T} - 19718.42660$ 
Which is the physically meaningful root?
> solve(delH_ig(T0,T)=Q,T);
                                     -3622.461198, 2.719888262, 1250.204886
```

2nd-virial description of the vapor

```
Now let's try it with a non-ideal vapor. Use 2nd virial coefficient given from correlation on page
89.
> B0 := Tr -> 0.083 - 0.422/Tr^1.6;
   B1 := Tr -> 0.139 - 0.172/Tr^4.2;
                                     B0 := Tr -> .083 - 0.422 / Tr1.6
                                     B1 := Tr -> .139 - 0.172 / Tr4.2
Critical properties, acentric factor of ammonia (from Table B.1)
> omega := 0.253;
   Tc := 405.7;
   Pc := 112.8;
                                     ω := .253
                                     Tc := 405.7
                                     Pc := 112.8
```

Here's the second virial coefficient, with its temperature dependence

```
> B := T -> R*Tc/Pc * (B0(T/Tc) + omega*B1(T/Tc));
```

$$B := T \rightarrow \frac{R T_c \left(B_0 \left(\frac{T}{T_c} \right) + \omega B_1 \left(\frac{T}{T_c} \right) \right)}{P_c}$$

Here we define the derivative dH/dP as a function of T. Note the need to use the "subs" construction. If you don't do it this way (i.e., if you just use T directly in the formula), you run into trouble when you try to evaluate the function for any value of T (more details in the following subsection)

```
> dHdP := T -> subs(t=T,B(t) - t*diff(B(t),t));
```

$$dHdP := T \rightarrow \text{subs} \left(t = T, B(t) - t \left(\frac{\partial}{\partial t} B(t) \right) \right)$$

⊕ *Here's some more detail on why the "subs" function is needed above*

Enthalpy change as a function of T0, T and P

```
> delH := (T0,T,P) -> delH_ig(T0,T) + (dHdP(T) - dHdP(T0)) * P;
```

$$\text{delH} := (T_0, T, P) \rightarrow \text{delH_ig}(T_0, T) + (dHdP(T) - dHdP(T_0)) P$$

Here's what the function looks like for our T0 and P = 1 bar

```
> delH(T0,T,1);
```

$$\begin{aligned} &.00008314000000 \frac{357800. T^2 + 151. T^3 + .1860000000 10^{10}}{T} - 19695.08706 - \frac{187995.0401}{T^{1.6}} \\ &- \frac{.1171698647 10^{12}}{T^{4.2}} - T \left(\frac{300792.0642}{T^{2.6}} + \frac{.4921134317 10^{12}}{T^{5.2}} \right) \end{aligned}$$

Solve gives more solutions than we want. Which one is physically relevant?

```
> solve(delH(T0,T,1)=Q,T);
```

```
35.07719292 - 32.46944714 I, 35.07719292 + 32.46944714 I,
```

```
-28.88056676 - 36.81301385 I, -28.88056676 + 36.81301385 I, 1249.912299
```

In this case it is expedient to work with fsolve, which attempts to return only a real (as opposed to complex) solution.

```
> fsolve(delH(T0,T,1)=Q,T);
```

$$\text{fsolve} \left(.00008314000000 \frac{357800. T^2 + 151. T^3 + .1860000000 10^{10}}{T} - 19695.08706 - \frac{187995.0401}{T^{1.6}} - \frac{.1171698647 10^{12}}{T^{4.2}} - T \left(\frac{300792.0642}{T^{2.6}} + \frac{.4921134317 10^{12}}{T^{5.2}} \right) = 37218, T \right)$$

But as you see, sometimes fsolve needs some help. You can direct it to a solution by specifying a range for it to work within

```
> fsolve(delH(T0,T,1)=Q,T,500..2000);
```

```
1249.912299
```

Let's examine the heat requirement as a function of pressure. Note that the 2nd-virial description probably breaks down beyond about 10 bar. Here's a loop that does the scan of pressure in a tidy fashion. The pressure scans 1, 10, 100, and 1000 bar.

```
> for i from 0 to 3 do
```

```
  print(10^i,fsolve(delH(T0,T,10^i)=Q,T,500..2000)) od;
```

```
1, 1249.912299
```

```
10, 1247.280510
```

```
100, 1221.120383
```

```
1000, 985.8500114
```

Remember the ideal-gas result was 1250.2 K. As you can see, there's really not much need to assume anything other than ideal-gas behavior for most cases of interest (i.e., less than 10 bar or

[[so).