Reif prob. 5.20

(0) Find the inversion curve for a van der waals gas.(1) Express your result in terms of the reduced variables p' and T', and find p' as a function of T' along the inversion curve. (2) Sketch this curve on a graph of p' versus T', being sure to indicate quantitatively the intercepts on the T' axis and the location of the maximum pressure on this curve

Before solve this problem, we have to solve 5.19

- Van der waals gas : $\left(p+\frac{a}{v^2}\right)(v-b)=R\,T$
- 'Critical point' of van der waals gas : a point where $(\partial^2 p/\partial v^2)_T=0$ in addition to $(\partial p/\partial v)_T=0$
- Temperature, pressure, molar volume of critical point: T_c, p_c, v_c
- a. Express a, b in terms of T_c and v_c

In[91]:= $p = \frac{R\,T}{v-b} - \frac{a}{v^2};$

firstder = $D\left[\frac{R\,T}{v-b} - \frac{a}{v^2}, v\right]$

Out[92]= $\frac{2\,a}{v^3} - \frac{R\,T}{(-b+v)^2}$

In[93]:= seconder = $D\left[\frac{R\,T}{v-b} - \frac{a}{v^2}, \{v, 2\}\right]$

Out[93]= $-\frac{6\,a}{v^4} + \frac{2\,R\,T}{(-b+v)^3}$

In[94]:= Solve[firstder == 0 && seconder == 0, {a, b}]

Out[94]= $\left\{\left\{a \to \frac{9\,R\,T\,v}{8}, b \to \frac{v}{3}\right\}\right\}$

Therefore, $a=\frac{9\,R\,T_c\,v_c}{8}$ and $b=\frac{v_c}{3}$. Save these values in 'abval'

In[95]:= abval = Solve[firstder == 0 && seconder == 0, {a, b}]

Out[95]= $\left\{\left\{a \to \frac{9\,R\,T\,v}{8}, b \to \frac{v}{3}\right\}\right\}$

- b. Express p_c in terms of T_c , v_c

Replace !

In[96]:= p /. abval

Out[96]= $\left\{\frac{3\,R\,T}{8\,v}\right\}$

- c. Write the van der waals equation in terms of the reduced dimensionless variables

$$T'=T/T_c,\quad v'=v/v_c,\quad p'=p/p_c$$

$(p + a\,v^{-2})\,(v - b) = R\,T$

$\left(p + \frac{9\,R\,T_c\,v_c}{8\,v^2}\right)\left(v - \frac{v_c}{3}\right) = R\,T$

$\left(p/p_c + \frac{9\,R\,T_c\,v_c}{8\,v^2}\,\frac{8\,v_c}{3\,R\,T_c}\right)\left(v/v_c - \frac{1}{3}\right) = R\,\frac{T}{p_c\,v_c}$

$\left(p/p_c + \frac{3\,{v_c}^2}{v^2}\right)\left(v/v_c - \frac{1}{3}\right) = \frac{8\,v_c}{3\,R\,T_c}\,\frac{R\,T}{v_c}$

$\left(p/p_c + \frac{3\,{v_c}^2}{v^2}\right)\left(v/v_c - \frac{1}{3}\right) = \frac{8\,T}{3\,T_c}$

$\left(p' + \frac{3}{v'^2}\right)\left(v' - \frac{1}{3}\right) = \frac{8}{3}\,T'$

- Finally, we have $\left(p' + \frac{3}{v'^2}\right)\left(v' - \frac{1}{3}\right) = \frac{8}{3}\,T'$ which involve neither a nor b

Now we are ready to solve 5.20

(0). Inversion curve ; when $\mu = \frac{v}{c_p}\left(\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p - 1\right) = 0 \to (\partial v/\partial T)_p = v/T$

since p is invariant, $d\,p = (\partial p/\partial T)_v\,\mathrm{dT} + (\partial p/\partial v)_T\,\mathrm{dv} = 0$

Recall that $p = \frac{R\,T}{v-b} - \frac{a}{v^2}$

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In[107]:= p = R T/(v - b) - a/v^2
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Out[107]= $-\frac{a}{v^2} + \frac{R\,T}{-b + v}$

$(\partial p/\partial T)_v$ is,

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In[109]:= dpdt = D[p, T]
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Out[109]= $\frac{R}{-b + v}$

$(\partial p/\partial v)_T$

```
In[110]:= dpdv = D[p, v]
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Out[110]= $\frac{2\,a}{v^3} - \frac{R\,T}{(-b + v)^2}$

$\left(\frac{\partial v}{\partial T}\right)_p$

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In[111]:= dvdt = FullSimplify[-dpdt / dpdv]
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Out[111]= $\frac{R\,v^3\,(-b + v)}{-2\,a\,(b - v)^2 + R\,T\,v^3}$

condition for inversion curve : $(\partial v/\partial T)_p = v/T$

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In[112]:= FullSimplify[dvdt == v/T]
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Out[112]= $\frac{R\,v^3\,(-b + v)}{-2\,a\,(b - v)^2 + R\,T\,v^3} == \frac{v}{T}$

(1) Express this result in terms of the reduced variables p' and T'

$\frac{R\,v^3\,(-b+v)}{-2\,a\,(b-v)^2 + R\,T\,v^3} == \frac{v}{T} \to \frac{2\,a}{R\,T}\left(\frac{v-b}{v}\right)^2 == b$

$\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 = b$
$\frac{2}{RT}\frac{9}{8}R\,T_c\,v_c\left(\frac{v-v_c/3}{v}\right)^2 = v_c/3$
$\frac{9}{4}(T_c/T)\left(1-\frac{v_c}{3v}\right)^2 = \frac{1}{3}$
$\left(1-\frac{1}{3v'}\right)^2 = \frac{4}{3}T'$

eliminate v' and putting the equation in terms of p' and T'

(note that $\left(p' + \frac{3}{v'^2}\right)\left(v' - \frac{1}{3}\right) = \frac{8}{3}T'$)

In[113]:= `Clear[p]`

In[42]:= $\texttt{sol = Solve}\left[\left(1-\frac{1}{3v}\right)^2 == \frac{4}{3}t, v\right]$

Out[42]= $\left\{\left\{v \to \frac{-3-2\sqrt{3}\sqrt{t}}{3(-3+4t)}\right\}, \left\{v \to \frac{-3+2\sqrt{3}\sqrt{t}}{3(-3+4t)}\right\}\right\}$

In[43]:= `sol = FullSimplify[sol]`

Out[43]= $\left\{\left\{v \to \frac{1}{3-2\sqrt{3}\sqrt{t}}\right\}, \left\{v \to \frac{1}{3+2\sqrt{3}\sqrt{t}}\right\}\right\}$

$\texttt{ptrela = }\left(\left(p+\frac{3}{v^2}\right)(v-1/3) == \frac{8t}{3}\right) \texttt{ /. sol}$

Out[60]= $\left\{\left(-\frac{1}{3}+\frac{1}{3-2\sqrt{3}\sqrt{t}}\right)\left(p+3\left(3-2\sqrt{3}\sqrt{t}\right)^2\right) == \frac{8t}{3},\right.$
$\left.\left(-\frac{1}{3}+\frac{1}{3+2\sqrt{3}\sqrt{t}}\right)\left(p+3\left(3+2\sqrt{3}\sqrt{t}\right)^2\right) == \frac{8t}{3}\right\}$

In[59]:= `psol1 = Simplify[Solve[ptrela[[1]], p]]`

Out[59]= $\left\{\left\{p \to -27+40\sqrt{3}\sqrt{t}-44t\right\}\right\}$

In[54]:= `psol2 = FullSimplify[Solve[ptrela[[2]], p]]`

Out[54]= $\left\{\left\{p \to -27-40\sqrt{3}\sqrt{t}-44t\right\}\right\}$

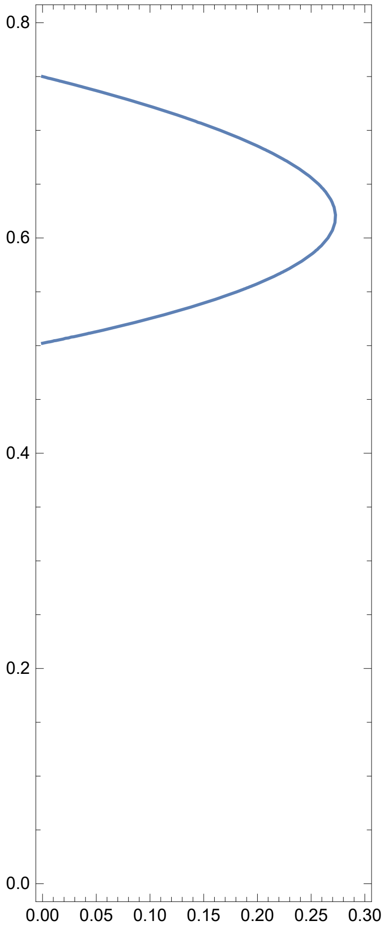
or,

In[79]:= $\texttt{Simplify}\left[p \texttt{ /. Solve}\left[\left(p+\frac{3}{v^2}\right)\left(v-\frac{1}{3}\right) == \frac{8}{3}t, p\right] \texttt{ /. sol}\right]$

Out[79]= $\left\{\left\{-27+40\sqrt{3}\sqrt{t}-44t\right\}, \left\{-27-40\sqrt{3}\sqrt{t}-44t\right\}\right\}$

In[118]:= ContourPlot$\left[-27+40\sqrt{3}\sqrt{t}-44t==p, \{p, 0, 0.3\}, \{t, 0, 0.8\}, \text{AspectRatio}\to\text{Automatic}\right]$

Out[118]=



Maximum & minimum temperature

In[121]:= Solve$\left[-27+40\sqrt{3}\sqrt{t}-44t==0, t\right]$

Out[121]= $\left\{\left\{t\to\frac{243}{484}\right\}, \left\{t\to\frac{3}{4}\right\}\right\}$

Temperature of maximum-pressure-point

In[120]:= Solve$\left[D\left[-27+40\sqrt{3}\sqrt{t}-44t, t\right]==0, t\right]$

Out[120]= $\left\{\left\{t\to\frac{75}{121}\right\}\right\}$

In[123]:=
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Show[
 {Graphics[{PointSize[0.02], Point[{-27 + 40 √3 √t - 44 t /. t → 75/121, 75/121}]}],
  ContourPlot[-27 + 40 √3 √t - 44 t == p, {p, 0, 0.3}, {t, 0, 0.8}]}]
```

Out[123]=