Quiz 8 March 5, 2020
Chemical Engineering Thermodynamics

Gasoline autoignites (explodes without a spark) in a mixture with oxygen at 560K (550°F). In an engine this condition leads to engine "ping" or "knock" on acceleration.

The 2014 Ferrari 458 Speciale engine has a **compression ratio of 14:1**. This ratio improves the engine efficiency and power and also reduces emissions. It might also lead to engine knock if the temperature on compression is too high (**> 560K**). Consider a fuel/air mixture **entering a cylinder at 20°C and 0.1 MPa**. Assume that the compression cycle is adiabatic and reversible. Use the equation of state $\boldsymbol{PV = RT + aP}$. The ideal gas heat capacity for the mixture does not depend on temperature and has a value of $\boldsymbol{C_p^{ig} = 13R}$ (where R = 8.13 cm^3 MPa/(mole K)). $a = R\,T_c/(8P_c)$ and T_c = 570 K; P_c = 2.5 MPa so **a = 237** cm^3/mol.

a) Compare this equation of state with the van der Waals equation of state:
$\boldsymbol{P = RT/(V-b) - a/V^2}$ and comment on the meaning of the term "a" in the proposed equation. Can this equation predict a liquid state and why?
b) Calculate the density of the initial state and of the final compressed state and put these in the table below.
c) Rewrite the equation of state to define P.
Also, define the compressibility ratio Z and $(\partial Z/\partial T)_\rho$.
Rewrite the equation of state to define V and $(\partial V/\partial T)_P$.
d) Write an equation that can be used to determine the final conditions after the compression based on the departure functions.
e) Use the following equations to determine two of the terms in part d using the equation of state.

$$\frac{(U-U^{ig})}{RT} = \int_0^\rho -T\left[\frac{\partial Z}{\partial T}\right]_\rho \frac{d\rho}{\rho}$$

$$\frac{(S-S^{ig})}{R} = \int_0^\rho \left[-T\left[\frac{\partial Z}{\partial T}\right] - (Z-1)\right]\frac{d\rho}{\rho} + \ln Z$$

$$\frac{(H-H^{ig})}{RT} = \int_0^\rho -T\left[\frac{\partial Z}{\partial T}\right]_\rho \frac{d\rho}{\rho} + Z - 1$$

$$\frac{(A-A^{ig})}{RT} = \int_0^\rho \frac{(Z-1)}{\rho}d\rho - \ln Z$$

$$\frac{(G-G^{ig})}{RT} = \int_0^\rho \frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z$$

f) Determine an expression for the other term in part d using T and P as parameters.
g) Solve for the final temperature by using your expression from part d. (Put the value for T_2 in the table.)
Will the gasoline autoignite under these conditions?
h) Determine the final P and the work that was required for this compression. (Put the value for P_2 in the table.)

a)

b)

	1	2
P, Mpa		
T, K		
ρ, mole/cm3		

c)

P =

Z =

$(\partial Z/\partial T)_\rho$ =

V =

$(\partial V/\partial T)_P$ =

d)

e)

f)

g) $T_2 =$

Autoignite?

h) $P_2 =$

$W =$

Answers: **Quiz 8 March 5, 2020**

a) The equation can be rearranged as P = RT/(V-a) so a is really "b" in the van der Waals equation which is the excluded volume, hence the units cm3/mole. This is a repulsive potential. You need an attractive potential to make a liquid state, that is you need the real "a" from the van der Waals equation which is 0 in this equation, so it can't make a liquid but has a boost in the pressure due to excluded volume. There is no attractive energy in this equation of state. From this alone you could ascertain that at constant pressure and temperature the internal energy, entropy, and enthalpy departure functions are 0.

b)

	1	**2**
P, Mpa	**0.1**	**2.03 or 2.08**
T, K	**293**	**370**
ρ, mole/cm3	**0.0000407 or 4.16e-5**	**0.000569 or 5.82e-4**

$$V = \frac{RT}{P} + a$$

$$\rho_1 = \frac{1}{V_1} = \frac{1}{\frac{RT_1}{P_1} + a}$$

$$= \frac{1}{\frac{8.31 \frac{J}{mol\,K}(293K)}{0.1MPa} + 237 \frac{cm^3}{mol}}$$

$$= 4.07e^{-5}\ cm^3/mol$$

$$\rho_2 = 14\rho_1 = 5.69e^{-4}\ cm^3/mol$$

c)

$$P = \frac{RT}{V-a}$$

$$Z = \frac{PV}{RT} = \frac{V}{V-a} = \frac{1}{1-a\rho}$$

$$(\partial Z/\partial T)_\rho = 0 \quad \text{No T dependence}$$

$$V = \frac{RT}{P} + a$$

$$(\partial V/\partial T)_P = \frac{R}{P}$$

d) Adiabatic + Reversible $\Delta S = 0$

$$\frac{\Delta S}{R} = \frac{(S-S^{is})_2}{R} - \frac{(S-S^{is})_1}{R} + \frac{S_2^{is} - S_1^{is}}{R}$$

e)

$$\frac{(s-s^{ig})}{R} = -\int_0^{\varepsilon}\left[-T\cancel{\left(\frac{\partial z}{\partial T}\right)_{\varepsilon}}^{\,0} - (z-1)\right]\frac{d\varepsilon}{\varepsilon} + \ln z$$

$$= -\int_0^{\varepsilon}\left(\left(\frac{1-a\varepsilon}{1-a\varepsilon}\right) - \frac{1}{1-a\varepsilon}\right)\frac{d\varepsilon}{\varepsilon} + \ln z$$

$$= -\int_0^{\varepsilon}\frac{-a\cancel{\varepsilon}}{1-a\varepsilon}\frac{d\varepsilon}{\cancel{\varepsilon}} + \ln z = \ln(1-a\varepsilon) + \ln\left(\frac{1}{1-a\varepsilon}\right) = 0$$

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f)

$$ds^{ig} = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP = c_p^{is}\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Maxwell relationship

$$= c_p^{is}\frac{dT}{T} - \frac{R\,dP}{P}$$

$$\Delta s^{is} = c_p^{is}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} = c_p^{is}\ln\frac{T_2}{T_1} - R\ln\left(\frac{T_2}{T_1}\left(\frac{V_1-a}{V_2-a}\right)\right)$$

$$= c_v^{is}\ln\frac{T_2}{T_1} - R\ln\left(\frac{V_2}{V_1}\right) - R\ln\left(\frac{z_2}{z_1}\right) \equiv 0$$

$$T_2 = T_1\exp\left(\frac{-R}{c_v}\left(\ln\frac{V_2}{V_1} + \ln\frac{z_2}{z_1}\right)\right)$$

$$= 293\text{K}\exp\left(-\frac{1}{12}\left(\ln\frac{1}{14} + \ln\left(\frac{1-237\frac{\text{cm}^3}{\text{mole}}\,4.07e^{-5}\frac{\text{mol}}{\text{cm}^3}}{1-237\frac{\text{cm}^3}{\text{mol}}\,5.69e^{-4}\frac{\text{mol}}{\text{cm}^3}}\right)\right)\right)$$

g) $T_2 =$ 360K $= 360\text{K}$

Autoignite? No

h) $P_2 =$ 2.07 MPa

$$P_2 = \frac{RT_2}{\frac{1}{\varepsilon_2} - a} = \frac{8.31\frac{\text{J}}{\text{K mole}}\,360\text{K}}{\frac{1}{5.69e^{-4}\frac{\text{mol}}{\text{cm}^3}} - 237\frac{\text{cm}^3}{\text{mol}}}$$

$$= 2.07\text{ MPa}$$

$W =$ $c_v(T_2 - T_1)$

$$= (12)\,8.31\frac{\text{J}}{\text{mol K}}(360\text{K} - 293\text{K})$$

$$= 7{,}580\ \text{J/mole}$$