(% i1) kill(all)$

peter.vlasschaert@gmail.com,16/06/2017 thermodynamics : 'Equation of State' 1e) virial gas equation state The virial gas equation of state (thrid order) ———————— ideal gases: P*V=R*T*n ,' n = number mole ' non-ideal gases: Z = (P*V)/(R*T),Z ' = compressibility factor ' z = Z1 = Z2

(% i1) p1:(a+b+c+d)^3;

(p1) $$(d+c+b+a)^3$$

(% i2) p2:expand(p1);

(1) $$p2|d^3+3c\,d^2+3b\,d^2+3a\,d^2+3c^2d+6bcd+6acd+3b^2d+6abd+3a^2d + c^3+3b\,c^2+3a\,c^2+3b^2c+6abc+3a^2c+b^3+3a\,b^2+3a^2b+a^3$$

(% i3) coeff(p2,d);

(% o3) $$3c^2+6bc+6ac+3b^2+6ab+3a^2$$

(% i4) p11:(P*V)/(R*T);

(p11) $$\frac{PV}{RT}$$

Z(V)=Z1=1+B/V+C/V^2+D/V^3 Z(P)=Z2=1+B1*P+C1*P^2+D1*P^3

(% i6) p3:Z1=1+B/V+C/V^2+D/V^3; p4:Z2=1+B1*P+C1*P^2+D1*P^3;

(p3) $$Z1=\frac{B}{V}+\frac{C}{V^2}+\frac{D}{V^3}+1$$

(p4) $$Z2=D1\,P^3+C1\,P^2+B1\,P+1$$

? P=P(T,Bi,Ci,Di,B,C,D) i=1,2,3....

(% i8) p5:ratsubst(p11, Z1, p3); p6:lhs(p5)*R*T/V=rhs(p5)*R*T/V;

(p5) $$\frac{PV}{RT}=\frac{V^3+B\,V^2+CV+D}{V^3}$$

(p6) $$P=\frac{RT\,\left(V^3+B\,V^2+CV+D\right)}{V^4}$$

(% i12) p(i):=coeff(radcan(num(rhs(p6))),V^i)*V^i/denom(rhs(p6)); p00:num(rhs(p6))$ p000:ev(p00,V=0)/denom(rhs(p6))$ pt:p000+p(1)+p(2)+p(3);

(2) $$o9|\mathrm{p}(i):=\frac{\mathrm{coeff}\left(\mathrm{radcan}\left(\mathrm{num}\left(\mathrm{rhs}\left(p6\right)\right)\right),V^i\right)\,V^i}{\mathrm{denom}\left(\mathrm{rhs}\left(p6\right)\right)}$$

(3) $$pt|\frac{RT}{V}+\frac{BRT}{V^2}+\frac{CRT}{V^3}+\frac{DRT}{V^4}$$

Z2=Z(T,V,Bi,Ci,Di,B,C,D) i=1,2,3...

(% i13) p7:subst(pt, P, p4);

(4)
$$p7|Z2 = B1\left(\frac{RT}{V}+\frac{BRT}{V^2}+\frac{CRT}{V^3}+\frac{DRT}{V^4}\right)+D1\left(\frac{RT}{V}+\frac{BRT}{V^2}+\frac{CRT}{V^3}+\frac{DRT}{V^4}\right)^3 + C1\left(\frac{RT}{V}+\frac{BRT}{V^2}+\frac{CRT}{V^3}+\frac{DRT}{V^4}\right)^2+1$$

(% i14) p8:expand(p7);

(5)
$$\begin{aligned}p8|Z2 = {} & \frac{B1RT}{V}+\frac{C1\,R^2\,T^2}{V^2}+\frac{B\,B1RT}{V^2}+\frac{D1\,R^3\,T^3}{V^3}+\frac{2B\,C1\,R^2\,T^2}{V^3}+\frac{B1CRT}{V^3}\\ & +\frac{3B\,D1\,R^3\,T^3}{V^4}+\frac{2C\,C1\,R^2\,T^2}{V^4}+\frac{B^2\,C1\,R^2\,T^2}{V^4}+\frac{B1DRT}{V^4}+\frac{3C\,D1\,R^3\,T^3}{V^5}\\ & +\frac{3B^2\,D1\,R^3\,T^3}{V^5}+\frac{2C1D\,R^2\,T^2}{V^5}+\frac{2BC\,C1\,R^2\,T^2}{V^5}+\frac{3D\,D1\,R^3\,T^3}{V^6}+\frac{6BC\,D1\,R^3\,T^3}{V^6}\\ & +\frac{B^3\,D1\,R^3\,T^3}{V^6}+\frac{2B\,C1D\,R^2\,T^2}{V^6}+\frac{C^2\,C1\,R^2\,T^2}{V^6}+\frac{6BD\,D1\,R^3\,T^3}{V^7}+\frac{3C^2\,D1\,R^3\,T^3}{V^7}\\ & +\frac{3B^2C\,D1\,R^3\,T^3}{V^7}+\frac{2C\,C1D\,R^2\,T^2}{V^7}+\frac{6CD\,D1\,R^3\,T^3}{V^8}+\frac{3B^2D\,D1\,R^3\,T^3}{V^8}\\ & +\frac{3B\,C^2\,D1\,R^3\,T^3}{V^8}+\frac{C1\,D^2\,R^2\,T^2}{V^8}+\frac{3D^2\,D1\,R^3\,T^3}{V^9}+\frac{6BCD\,D1\,R^3\,T^3}{V^9}+\frac{C^3\,D1\,R^3\,T^3}{V^9}\\ & +\frac{3B\,D^2\,D1\,R^3\,T^3}{V^{10}}+\frac{3C^2D\,D1\,R^3\,T^3}{V^{10}}+\frac{3C\,D^2\,D1\,R^3\,T^3}{V^{11}}+\frac{D^3\,D1\,R^3\,T^3}{V^{12}}+1\end{aligned}$$

new Z2 with old Z1 : coefficient comparing part 1 : new Z2

(% i16) for i:1 thru 12 do pp(i):=subst(x^i, 1/V^i, p8)$ ppp(i):=coeff(rhs(pp(i)),x^(i))$

(% i18) pp(2); ppp(2);

(6)
$$\begin{aligned}o17|Z2 = {} & C1\,R^2\,T^2\,x^2+B\,B1RT\,x^2+\frac{B1RT}{V}+\frac{D1\,R^3\,T^3}{V^3}+\frac{2B\,C1\,R^2\,T^2}{V^3}+\frac{B1CRT}{V^3}\\ & +\frac{3B\,D1\,R^3\,T^3}{V^4}+\frac{2C\,C1\,R^2\,T^2}{V^4}+\frac{B^2\,C1\,R^2\,T^2}{V^4}+\frac{B1DRT}{V^4}+\frac{3C\,D1\,R^3\,T^3}{V^5}\\ & +\frac{3B^2\,D1\,R^3\,T^3}{V^5}+\frac{2C1D\,R^2\,T^2}{V^5}+\frac{2BC\,C1\,R^2\,T^2}{V^5}+\frac{3D\,D1\,R^3\,T^3}{V^6}+\frac{6BC\,D1\,R^3\,T^3}{V^6}\\ & +\frac{B^3\,D1\,R^3\,T^3}{V^6}+\frac{2B\,C1D\,R^2\,T^2}{V^6}+\frac{C^2\,C1\,R^2\,T^2}{V^6}+\frac{6BD\,D1\,R^3\,T^3}{V^7}+\frac{3C^2\,D1\,R^3\,T^3}{V^7}\\ & +\frac{3B^2C\,D1\,R^3\,T^3}{V^7}+\frac{2C\,C1D\,R^2\,T^2}{V^7}+\frac{6CD\,D1\,R^3\,T^3}{V^8}+\frac{3B^2D\,D1\,R^3\,T^3}{V^8}\\ & +\frac{3B\,C^2\,D1\,R^3\,T^3}{V^8}+\frac{C1\,D^2\,R^2\,T^2}{V^8}+\frac{3D^2\,D1\,R^3\,T^3}{V^9}+\frac{6BCD\,D1\,R^3\,T^3}{V^9}+\frac{C^3\,D1\,R^3\,T^3}{V^9}\\ & +\frac{3B\,D^2\,D1\,R^3\,T^3}{V^{10}}+\frac{3C^2D\,D1\,R^3\,T^3}{V^{10}}+\frac{3C\,D^2\,D1\,R^3\,T^3}{V^{11}}+\frac{D^3\,D1\,R^3\,T^3}{V^{12}}+1\end{aligned}$$

(% o18) $C1\,R^2\,T^2+B\,B1RT$

part 2 : old Z1

(% i20) for i:1 thru 4 do qq(i):=subst(x^i, 1/V^i, p3)$ qqq(i):=coeff(rhs(qq(i)),x^(i))$

(% i22) qq(2); qqq(2);

(% o21) $$Z1 = C\,x^2 + \frac{B}{V} + \frac{D}{V^3} + 1$$

(% o22) $$C$$

coefficient : old Z2 ('p4')

(% i25) q1:part(solve(ppp(1)=qqq(1),B1),1); q2:part(solve(ppp(2)=qqq(2),C1),1); q3:part(solve(ppp(3)=qqq(3),D1),1);

(q1) $$B1 = \frac{B}{RT}$$

(q2) $$C1 = -\frac{B\,B1\,RT - C}{R^2\,T^2}$$

(q3) $$D1 = -\frac{2B\,C1\,R^2\,T^2 + B1\,C\,RT - D}{R^3\,T^3}$$

(% i28) qq1:q1; qq2:ev(q2,q1); qq3:ev(q3,q1,qq2);

(qq1) $$B1 = \frac{B}{RT}$$

(qq2) $$C1 = -\frac{B^2 - C}{R^2\,T^2}$$

(qq3) $$D1 = -\frac{-D + BC - 2B\,\left(B^2 - C\right)}{R^3\,T^3}$$

find : Z2=Z(P,T,C,B,D)

(% i29) pq:ev(p4,qq1,qq2,qq3);

(7) $$pq|Z2 = \frac{BP}{RT} - \frac{\left(B^2 - C\right)\,P^2}{R^2\,T^2} - \frac{\left(-D + BC - 2B\,\left(B^2 - C\right)\right)\,P^3}{R^3\,T^3} + 1$$

general : v=volume p=pressure Z=compressibility factor n= integer ———————— Z=1+sum(a(i)*1/v^i,i=1..n) z=1+sum(a1(i)*p^i ,i=1..n) ————————