Analysis of thermodynamic for an Equation of State (EoS)

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1 Purpose of the analysis

This paper analyses the thermodynamic coefficients of a system in order to set-up some parameters used in the Equation of State (EoS) for any phase of pure fluid: solid, liquid, gas (not only for perfect gas). However, equilibrium between phases like liquid-vapour is not managed.
As usually, one starts with equations using extensive variables U in J , V in m3, etc. (which depends on the system size) in contrast with specific and intensive quantities v in m^3/kg, ρ in kg/m^3, u, h in J/kg, s in J/K/kg (which does not depends on the system size, and written with lower case).

2 Basic tools: Useful cyclic sequence x, y, z , Maxwell rule

Considering 3 independent variables. When there is an EoS function $f(x,y,z) = 0$, one can consider each variable as dependant on the 2 others $x(y,z)$, $y(z,x)$, $z(x,y)$. In those conditions one has:

Useful cyclic sequence $\boxed{x,y,z}$: $\boxed{\frac{\partial x}{\partial y}_{|z} \frac{\partial y}{\partial z}_{|x} \frac{\partial z}{\partial x}_{|y} = -1}$ Example: starting with $\frac{\partial p}{\partial T}_{|V}$ a valid sequence is p, T, V .

Proof : From $dx = \frac{\partial x}{\partial y}_{|z} dy + \frac{\partial x}{\partial z}_{|y} dz$ and $dy = \frac{\partial y}{\partial z}_{|x} dz + \frac{\partial y}{\partial x}_{|z} dx$ ...

with dy substitution $dx = \frac{\partial x}{\partial y}_{|z} \left(\frac{\partial y}{\partial z}_{|x} dz + \frac{\partial y}{\partial x}_{|z} dx \right) + \frac{\partial x}{\partial z}_{|y} dz$ so $dx = \underbrace{\left(\frac{\partial x}{\partial y}_{|z} \frac{\partial y}{\partial z}_{|x} + \frac{\partial x}{\partial z}_{|y} \right)}_{=0} dz + \underbrace{\frac{\partial x}{\partial y}_{|z} \frac{\partial y}{\partial x}_{|z}}_{=1 \text{ obvious}} dx$

So $\frac{\partial x}{\partial y}_{|z} \frac{\partial y}{\partial z}_{|x} = -\frac{\partial x}{\partial z}_{|y}$ which is the cyclic $\frac{\partial x}{\partial y}_{|z} \frac{\partial y}{\partial z}_{|x} \frac{\partial z}{\partial x}_{|y} = -1$ with the sequence x, y, z occurring in the numerators as in $\frac{\partial x}{\partial y}_{|z}$.

Maxwell rule : $\boxed{dF = Ady + Bdz}$ with $A = \frac{\partial F}{\partial y}_{|z}$ and $B = \frac{\partial F}{\partial z}_{|y}$ imply $\boxed{\frac{\partial A}{\partial z}_{|y} = \frac{\partial B}{\partial y}_{|z}}$ for an exact differential.

Proof : For an exact differential or state function $F(y,z) = \int dF$. One can write $dF = \frac{\partial F}{\partial y}_{|z} dy + \frac{\partial F}{\partial z}_{|y} dz$ and the second derivatives $\frac{\partial^2 F}{\partial y \partial z} = \frac{\partial \frac{\partial F}{\partial y}_{|z}}{\partial z}_{|y}$ and $\frac{\partial^2 F}{\partial z \partial y} = \frac{\partial \frac{\partial F}{\partial z}_{|y}}{\partial y}_{|z}$. The second derivatives rule for exact differential is $\frac{\partial^2 F}{\partial y \partial z} = \frac{\partial^2 F}{\partial z \partial y}$ which prove it.
This is used when first partial derivatives are "quite hidden" equal to some variable or functions A, B like in $dF = Ady + Bdz$.

Partial derivative: f being a state function of 3 variables x, y, z . Its total differential is: $df = \frac{\partial f}{\partial x}_{|y,z} dx + \frac{\partial f}{\partial y}_{|z,x} dy + \frac{\partial f}{\partial z}_{|x,y} dz$ The partial derivative of f wrt y with z keept constant is written as $\frac{\partial f}{\partial y}_{|z}$. But this is also the value of df divided by the value dy such z kept constant $dy_{|z}$. So $\frac{df}{dy_{|z}} = \frac{\partial f}{\partial y}_{|z}$. Idem for $\frac{dx}{dy_{|z}}, \frac{dy}{dy_{|z}}$ written as $\frac{\partial x}{\partial y}_{|z}, \frac{\partial y}{\partial y}_{|z}$ and in such conditions $dz = 0$.

That gives: $\frac{\partial f}{\partial y}_{|z} = \frac{\partial f}{\partial x}_{|y,z} \frac{\partial x}{\partial y}_{|z} + \frac{\partial f}{\partial y}_{|x,z} \underbrace{\frac{\partial y}{\partial y}_{|z}}_{=1} + \frac{\partial f}{\partial z}_{|x,y} \underbrace{\frac{\partial z}{\partial y}_{|z}}_{=0}$ With the condition $\frac{\partial f}{\partial x}_{|y,z} = \frac{\partial f}{\partial x}_{|y}, \frac{\partial f}{\partial y}_{|x,z} = \frac{\partial f}{\partial y}_{|x}$ ➔ $\boxed{\frac{\partial f}{\partial y}_{|z} = \frac{\partial f}{\partial x}_{|y} \frac{\partial x}{\partial y}_{|z} + \frac{\partial f}{\partial y}_{|x}}$*

* One gets the same identity for f function of 2 variables $f(x,y)$ and for a third parameter z kept constant, without the condition.

3 Recall 1st principle

With the kinetic energy of the system $Ek = 0.5mv^2$ (in J) and with its potential energy $Ep = -\vec{F}.\vec{r}$

(note $\vec{F} = -\vec{\nabla}Ep$, for $\vec{z}$ oriented from ground to sky, Ep due to gravitation increases with z "$Ep = mgz$")

1st principle equation for internal energy: $dU_T = d(U + Ek + Ep) = \delta Q + \delta W$

where δQ, δW represent variations in heat energy and mechanical work (algebraic values in J) which are inexact differential (path dependent quantities with δ contrary to exact differential or state function depending onlyon final and initial points like dU), δQ, δW do not correspond in general to any difference. The conventional rule for those algebraic values is taken as positive for what the system receives from the external, and negative for what the system produces and gives to the externalor transfer to the external.

Generally, Ek and Ep variations are null, hence $dU = \delta Q + \delta W$ (in J) . If Ek is not null, $dU = \delta Q + \delta W - dEk$

- With variables p, V, T linked together by an EoS $p = p(V, T)$, one can write for quasi-static transformation in mechanical equilibrium $Ek = 0$, with work from pressure $\delta W = -pdV$ and one can write obviously in all generalities δQ as a non-state function of two independent variables (T, V) : $\delta Q = \boldsymbol{C_v}dT + ldV$ hence $dU = \boldsymbol{C_v}dT + (l - p)dV$ (in J)
- As an exact differential, $dU = \frac{\partial U}{\partial T}_{|V} dT + \frac{\partial U}{\partial V}_{|T} dV$ shows as expected that $\boldsymbol{C_V} = \frac{\partial U}{\partial T}_{|V}$ (in J/K)
- Similarly, with $\delta Q = \boldsymbol{C_p}dT + kdp$, $d(U + pV) = dH = \boldsymbol{C_p}dT + (k + V)dp$ shows $\boldsymbol{C_p} = \frac{\partial H}{\partial T}_{|p}$ (in J/K)

4 Recall 2nd principle

For reversible process with a heat transfer δQ^r there is a relation $\delta Q^r = T.dS$ which is the fundamental equation for the state function entropy (in J/K).

- With variables p, V, T linked together by an EoS $p = p(V, T)$, with $\delta Q^r = \boldsymbol{C_v}dT + ldV = T.dS$ $dS = \frac{\boldsymbol{C_v}}{T}dT + \frac{l}{T}dV$ where $\frac{l}{T} = \frac{\partial S}{\partial V}_{|T}$ (J/K/m3) . In combination with 1st principle, $dU = T.dS - pdV$.

Similar equations occurs writing $\delta Q^r = \boldsymbol{C_p}dT + kdp = T.dS$: $dS = \frac{\boldsymbol{C_p}}{T}dT + \frac{k}{T}dp$, $\frac{k}{T} = \frac{\partial S}{\partial p}_{|T}$ (in J/K/Pa)

and with 1st principle for the enthalpy: $d(U + pV) = dH = T.dS + Vdp$

5 Recall material properties:

- Coefficient of thermal expansion (at constant pressure p) $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}_{|p}$ (in 1/K)
- Compressibility (at constant temperature T) $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}_{|T}$ (or at constant entropy κ_S etc.) (in 1/Pa)
- Bulk modulus $B = \frac{1}{\kappa_T} = -V\frac{\partial p}{\partial V}_{|T}$ used for water hammers: $\Delta p = B\Delta V = a.\rho.\Delta vel$

5.1 Relations obvious from volume V to specific intensive quantities density $\rho = m/V$

- $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}_{|p} = \frac{\rho V}{mV}\frac{\partial V}{\partial T}_{|p} = \rho\frac{\partial V/m}{\partial T}_{|p} = \rho\frac{\partial 1/\rho}{\partial T}_{|p} = -\frac{\rho}{\rho^2}\frac{\partial \rho}{\partial T}_{|p}$ $\alpha = -\frac{1}{\rho}\frac{\partial \rho}{\partial T}_{|p}$ (called β in ESPSS)
- $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}_{|T}$ idem => $\kappa_T = \frac{1}{\rho}\frac{\partial \rho}{\partial p}_{|T}$ $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial p}_{|S}$ idem => $\kappa_S = \frac{1}{\rho}\frac{\partial \rho}{\partial p}_{|S}$ (in 1/K)
- Sound velocity $a^2 = \frac{\partial p}{\partial \rho}_{|S}$ i.e. $a^2 = \frac{1}{\rho\kappa_S}$ (in m/s)

5.2 Better evaluation of the terms l/T , k/T used for Mayer's and Reech's relations

Considering the function $F = U - TS$: $d(U - TS) = dU - d(TS) = \sout{T.dS} - pdV - SdT \sout{- TdS}$ hence $d(U - TS) = -pdV - SdT$ is an exact differential of the function of $F(V, T)$: $-p = \frac{\partial F}{\partial V}_{|T}$ and $-S = \frac{\partial F}{\partial T}_{|V}$, the second derivative identity rule (Maxwell) for F gives $\frac{\partial -p}{\partial T}_{|V} = \frac{\partial -S}{\partial V}_{|T}$ i.e. $\frac{\partial p}{\partial T}_{|V} = \frac{\partial S}{\partial V}_{|T}$ then $\frac{l}{T} = \frac{\partial p}{\partial T}_{|V}$

Similarly $G = U + PV - TS$: $d(U + PV - TS) = dH - d(TS) = \sout{T.dS} + Vdp - SdT \sout{- TdS}$ $\frac{\partial V}{\partial T}_{|p} = \frac{\partial -S}{\partial p}_{|T}$ $\frac{k}{T} = -\frac{\partial V}{\partial T}_{|p}$ $\frac{k}{T} = -V\alpha$

5.3 Entropy equation

$dS = \frac{\boldsymbol{C_v}}{T}dT + \frac{\partial p}{\partial T}_{|V}dV$ (in J/K) also $dS = \frac{\boldsymbol{C_p}}{T}dT - \frac{\partial V}{\partial T}_{|p}dp$ (in J/K) $\frac{\partial p}{\partial T}_{|V}$ or $-\frac{\partial V}{\partial T}_{|p}$ come from EoS.

EoS $pV = nRT, \frac{\partial p}{\partial T}_{|V} = \frac{R}{V}, -\frac{\partial V}{\partial T}_{|p} = -\frac{R}{p}$: $S(T,V) = \boldsymbol{C_v} \ln T + nR \ln V + S_{oTV}$; $S(T,p) = \boldsymbol{C_p} \ln T - nR \ln p + S_{oTp}$ are equal if $S_{oTV} = -nR \ln nR$, $S_{oTp} = 0$ (J/K)

Because $S(T,V) = \boldsymbol{C_v} \ln T + nR \ln V - nR \ln nR = (\boldsymbol{C_p} - nR) \ln T + nR \ln \frac{nRT}{p} - nR \ln nR = \boldsymbol{C_p} \ln T - nR \ln p = \boldsymbol{C_p} \ln T - nR \ln p = S(T,p)$ (in J/K).

But $S(T,V) = \boldsymbol{C_v} \ln {}^{T}/_{To} + nR \ln {}^{V}/_{Vo}$ $\quad S_{oTV} = (\boldsymbol{C_p} - nR) \ln {}^{T}/_{To} + nR \ln \frac{Tpo}{pTo}$ $\quad S_{oTV} = \boldsymbol{C_p} \ln {}^{T}/_{To} - nR \ln \frac{p}{po}$

5.4 Mayer' s relations $\boldsymbol{C_p - C_v}$ and Reech's formula

Mayer's relation is $\boldsymbol{C_p - C_v} = T \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p}$ i.e. $\boldsymbol{C_p - C_v} = TV \frac{\alpha^2}{\kappa_T}$ (in J/K) valid for pure fluid: solid, liquid, gas (not only for perfect gas: EoS $pV = nRT, \boldsymbol{C_p - C_v} = T \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p}$ $\quad \frac{\partial p}{\partial T}_{|V} = \frac{nR}{V}$ $\quad \frac{\partial V}{\partial T}_{|p} = \frac{nR}{p}$ $\quad \boldsymbol{C_p - C_v} = T \frac{nR}{V} \frac{nR}{p} = nR$)

Proof : $dS = \frac{C_v}{T} dT + \frac{\partial p}{\partial T}_{|V} dV$ with $dV = \frac{\partial V}{\partial T}_{|p} dT + \frac{\partial V}{\partial p}_{|T} dp$ gives $dS = \frac{C_v}{T} dT + \frac{\partial p}{\partial T}_{|V} \left(\frac{\partial V}{\partial T}_{|p} dT + \frac{\partial V}{\partial p}_{|T} dp \right)$

$dS = \left(\frac{C_v}{T} + \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p} \right) dT + \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial p}_{|T} dp$ compared with $dS = \frac{C_p}{T} dT - \frac{\partial V}{\partial T}_{|p} dp$ so $\frac{C_v}{T} + \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p} = \frac{C_p}{T}$

$\boldsymbol{C_p - C_v} = T \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p}$, cyclic sequence p, T, V gives $\frac{\partial p}{\partial T}_{|V} \frac{\partial T}{\partial V}_{|p} \frac{\partial V}{\partial p}_{|T} = -1$, $\frac{\partial p}{\partial T}_{|V} = -\frac{\frac{\partial V}{\partial T}_{|p}}{\frac{\partial V}{\partial p}_{|T}}$ thus $T \frac{\partial p}{\partial T}_{|V} \frac{\partial V}{\partial T}_{|p} = T \frac{V^2 \alpha^2}{V \kappa_T}$

Reech's formula with $\frac{\boldsymbol{C_p}}{\boldsymbol{C_v}} = \gamma$: $\gamma = \frac{\kappa_T}{\kappa_S}$ valid for pure fluid: solid, liquid, gas (not only for perfect gas).

Because $dS = \frac{C_v}{T} dT + \frac{\partial p}{\partial T}_{|V} dV = \frac{C_p}{T} dT - \frac{\partial V}{\partial T}_{|p} dp$, in an isentropic process, $dS = 0$ $dT = -\frac{T}{C_v} \frac{\partial p}{\partial T}_{|V} dV = \frac{T}{C_p} \frac{\partial V}{\partial T}_{|p} dp$

so still because $dS = 0$ one can write $\frac{dV}{dp}$ as $\frac{\partial V}{\partial p}_{|S}$ which lead to $\frac{dV}{dp} = \frac{\partial V}{\partial p}_{|S} = -\frac{C_v}{C_p} \frac{\partial V}{\partial T}_{|p} \frac{\partial T}{\partial p}_{|V}$

Because cyclic sequence V, T, p gives $\frac{\partial V}{\partial T}_{|p} \frac{\partial T}{\partial p}_{|V} \frac{\partial p}{\partial V}_{|T} = -1$ $\quad \frac{\partial V}{\partial T}_{|p} \frac{\partial T}{\partial p}_{|V} = -\frac{\partial V}{\partial p}_{|T}$ so $\frac{\partial V}{\partial p}_{|S} = \frac{C_v}{C_p} \frac{\partial V}{\partial p}_{|T}$ so $\kappa_S \gamma = \kappa_T$

5.5 Sound velocity

Thanks to Reech, $a^2 = \frac{1}{\rho \kappa_S} = \frac{\gamma}{\rho \kappa_T}$ so $\gamma = a^2 \rho \kappa_T$ or $\kappa_T = \frac{\gamma}{\rho a^2}$ (as in ESPSS)

5.6 A relation for $\boldsymbol{C_v}$ from $\boldsymbol{C_p}$ and a^2 sound velocity

From Mayer $\boldsymbol{C_p - C_v} = TV \frac{\alpha^2}{\kappa_T}$ (in J/K) , using Reech $\boldsymbol{C_p - C_v} = TV \rho a^2 \frac{\alpha^2}{\gamma}$

$\boldsymbol{C_p - C_v} = \boldsymbol{C_v} TV \rho a^2 \frac{\alpha^2}{\boldsymbol{C_p}}$ $\quad \boldsymbol{C_p} = \boldsymbol{C_v} \left(1 + TV \rho a^2 \frac{\alpha^2}{\boldsymbol{C_p}} \right)$ This gives $\boldsymbol{C_v} = \frac{\boldsymbol{C_p}}{\left(1 + TV \rho a^2 \frac{\alpha^2}{\boldsymbol{C_p}}\right)}$ (in J/K)

With ρV being a specific mass, $c_v = \frac{c_p}{\left(1 + T\, a^2 \frac{\alpha^2}{c_p}\right)}$ (in J/K/kg) (as in ESPSS)

6 EoS

With variables p, ρ, T the EoS can be written as $p = p(\rho, T)$ or $\rho = \rho(p, T)$.

With this last form, $d\rho = \frac{\partial \rho}{\partial T}_{|p} dT + \frac{\partial \rho}{\partial p}_{|T} dp$. So $d\rho = -\rho \alpha dT + \rho \kappa_T dp$ $\left(\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}_{|p} \right.$ and $\left. \kappa_T = \frac{1}{\rho} \frac{\partial \rho}{\partial p}_{|T} \right)$

- For constant temperature, $dT = 0$, and with κ_T computed for the same temperature with the sound velocity at T, this gives $\rho_{(p,T)} = \rho_{(p_o,T)} (1 + \kappa_T (p - p_o))$ (as in ESPSS with $p_o = 0$)

- More generally, $\rho_{(p,T)} = \rho_{(p_o,T_o)} (1 + \kappa_T . (p - p_o) - \alpha . (T - T_o))$ with κ_T computed for the temperature T and α computed for the pressure p, (α versus p is not available for ESPSS perfect fluids).

Other State functions

Enthalpy :with $dH = \boldsymbol{C_p} dT + (k + V) dp$ (in J) i.e $dh = c_p dT + \frac{1}{\rho} (1 - T\alpha) dp$ (in J/kg) and assuming no effects of the pressure, so for all pressures, $h = h_o + \int_{T_o}^{T} c_p dT$ (in ESPSS T_o is the first triple point T of the perfect fluid table, $h_o = 0$).

Entropy : $dS = \frac{\boldsymbol{C_p}}{T} dT - \frac{\partial V}{\partial T}_{|p} dp$ or $dS = \frac{\boldsymbol{C_p}}{T} dT + V\alpha dp$ (in J/K) i.e $ds = \frac{c_p}{T} dT + \frac{\alpha}{\rho} dp$ (in J/K/kg) ,

$s = s_o + \int_{T_o}^{T} \frac{c_p}{T} dT + \int_{p_o}^{p} \frac{\alpha}{\rho} dp$ (in ESPSS T_o is the first triple point T of the perfect fluid table, $p_o = 0, s_o = 0$)

Note on the interpolation functions: generally linear (or few order) interpolations are valid, exemple for $h(p,T)$. But for entropy, it has been found that log-log interpolation gives better results for $s(p,T)$ or $s(p,h)$ and it has been found that lin-hyperbolic gives better results for $\rho(p,T)$ and lin-log interpolation should give better results for $h(p,s)$ etc..., see "Eco-Kci-Me-111 Thermo_Interpol01.pdf"

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> *La thermodynamique est une discipline étrange... La première fois que vous la découvrez, vous ne comprenez rien... La deuxième fois, vous pensez que vous comprenez, sauf un ou deux points... La troisième fois, vous savez que vous ne comprenez plus rien, mais à ce niveau vous êtes tellement habitué que ça ne vous dérange plus. attribué à Arnold Sommerfeld, vers 1940*
