Thermodynamics Relations

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Mathematical Theorems

- If there exists a relation among $x,\ y\ \&\ z;\ \longrightarrow f(x,y,z)=0$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y=-1}$$

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial y}\right)_z=\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial y}\right)_x=\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y=1}$$

- $f(x,y,z)=0 \longmapsto z=z(x,y),\ \ y=y(z,x),\ \ x=x(y,z)$

$$z=z(x,y)\rightarrow dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy=Mdx+Ndy$$

For continuous functions, $\frac{\partial^2 z}{\partial x \partial y}=\frac{\partial^2 z}{\partial y \partial x}\Rightarrow \boxed{\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y}$

Maxwell’s Relationships

- Internal Energy, $du=\partial q+\partial w=Tds-Pdv$ (for rev. process)
- Enthalpy, $h\equiv u+Pv\Rightarrow dh=du+Pdv+vdP=Tds+vdP$
- Helmholtz Energy, $f\equiv u-Ts\Rightarrow df=-Pdv-sdT$
- Gibbs Energy, $g\equiv h-Ts\Rightarrow dg=dh-Tds-sdT=vdP-sdT$

For continuous functions, $\frac{\partial^2 z}{\partial x \partial y}=\frac{\partial^2 z}{\partial y \partial x}\Rightarrow\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y$

1. $du=+Tds-Pdv\Rightarrow\boxed{\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{\partial P}{\partial s}\right)_v}$ .... (M01)
2. $dh=+Tds+vdP\Rightarrow\boxed{\left(\frac{\partial T}{\partial P}\right)_s=+\left(\frac{\partial v}{\partial s}\right)_P}$ .... (M02)
3. $df=-sdT-Pdv\Rightarrow\boxed{\left(\frac{\partial s}{\partial v}\right)_T=+\left(\frac{\partial P}{\partial T}\right)_v}$ .... (M03)
4. $dg=-sdT+vdP\Rightarrow\boxed{\left(\frac{\partial s}{\partial P}\right)_T=-\left(\frac{\partial v}{\partial T}\right)_P}$ .... (M04)

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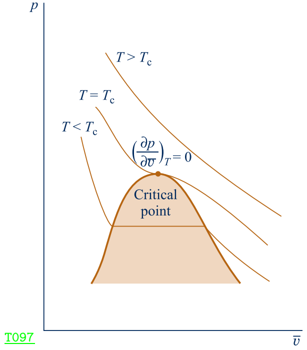
van der Waals’ Equation

$$\boxed{P=\frac{RT}{v-b}-\frac{a}{v^2}}$$

- $b\Rightarrow$ account for the volume occupied by gas molecules
- $a\Rightarrow$ account for intermolecular forces of attraction.



At critical point: $\left(\frac{\partial P}{\partial v}\right)_T=\left(\frac{\partial^2 P}{\partial v^2}\right)_T=0$
$\Rightarrow v_c=3b,\ \ a=\frac{27}{64}\frac{R^2T_c^2}{P_c},\ \ b=\frac{RT_c}{8P_c}$
$\Rightarrow Z_c=\frac{P_cv_c}{RT_c}=\frac{3}{8}=0.375$

C_v & Thermodynamics Relationships

- $du = Tds - Pdv \Rightarrow \left(\frac{\partial u}{\partial s}\right)_v = T$
- $C_v \equiv \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v$
- $\left(\frac{\partial C_v}{\partial v}\right)_T = \frac{\partial}{\partial v}\left[T\left(\frac{\partial s}{\partial T}\right)_v\right] = T\frac{\partial^2 s}{\partial v \partial T} = T\frac{\partial}{\partial T}\left[\frac{\partial s}{\partial v}\right]_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$
  using Maxwell's relation: $\left(\frac{\partial s}{\partial v}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_v$

If P-v-T data or mathematical relationship is available, it is possible to evaluate $\partial^2 P/\partial T^2$, and then $(\partial C_v/\partial v)_T$.

- Ideal gas: $Pv = RT$
  $\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v},\ \left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0 \longmapsto C_v \neq f(v)$
- van der Wall's gas: $P = \frac{RT}{v-b} - \frac{a}{v^2}$
  $\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b},\ \left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0 \longmapsto C_v \neq f(v)$

C_P & Thermodynamics Relationships

- $dh = Tds + vdP \Rightarrow \left(\frac{\partial h}{\partial s}\right)_P = T$
- $C_P = \left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial T}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_P$
- $\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P}\left[T\left(\frac{\partial s}{\partial T}\right)_P\right] = T\frac{\partial}{\partial T}\left[\frac{\partial s}{\partial P}\right]_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$
  using Maxwell's relation: $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$
- Ideal gas: $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P},\ \ \left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0 \longmapsto C_P \neq f(P)$
- van der Wall's gas: $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P - \frac{a}{v^2}\left(1 - \frac{2b}{v}\right)}$
  $\left(\frac{\partial^2 v}{\partial T^2}\right)_P = -\frac{R^2\left(\frac{2a}{v^3} - \frac{6ab}{v^4}\right)}{\left(P - \frac{a}{v^2}\left(1 - \frac{2b}{v}\right)\right)^3} \longmapsto C_P = f(P)$

Tds Relationships

- $s = s(v, T) \longrightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$
  $C_v = T\left(\frac{\partial s}{\partial T}\right)_v$ & $\left(\frac{\partial s}{\partial v}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_v$, Maxwell's Relation (C)
  $\boxed{Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv}$ .... (1^{st} Tds)
- $s = s(P, T) \longrightarrow ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$
  $C_P = T\left(\frac{\partial s}{\partial T}\right)_P$ & $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$, Maxwell's Relation (D)
  $\boxed{Tds = C_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP}$ .... (2^{nd} Tds)
- $s = s(P, v) \longrightarrow ds = \left(\frac{\partial s}{\partial P}\right)_v dP + \left(\frac{\partial s}{\partial v}\right)_P dv$
  $C_v = T\left(\frac{\partial s}{\partial T}\right)_v$ & $C_P = T\left(\frac{\partial s}{\partial T}\right)_P$
  $\boxed{Tds = C_v\left(\frac{\partial T}{\partial P}\right)_v dP + C_P\left(\frac{\partial T}{\partial v}\right)_P dv}$ .... (3^{rd} Tds)

Internal Energy, u

- $u = u(v, T) \longrightarrow du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$
- $du = Tds - Pdv = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv - Pdv$ ($\hookleftarrow$ 1^{st} Tds Eq.)
  $\boxed{\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P}$
  $\boxed{du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv}$
- Ideal gas: $\left(\frac{\partial u}{\partial v}\right)_T = \left[\frac{RT}{v} - P\right] = 0$
  $\left(\frac{\partial u}{\partial v}\right)_T = 0 = \left(\frac{\partial u}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v}\left(\frac{\partial u}{\partial P}\right)_T \rightarrow \left(\frac{\partial u}{\partial P}\right)_T = 0$
  $\left(\frac{\partial u}{\partial v}\right)_T = 0 \longrightarrow u \neq f(v)$: $\qquad \left(\frac{\partial u}{\partial P}\right)_T = 0 \rightarrow u \neq f(P)$

$$\longrightarrow du = C_v dT = f(T)$$

- van der Waals' gas:
  $\left(\frac{\partial u}{\partial v}\right)_T = \frac{RT}{v-b} - P = \frac{a}{v^2} \longrightarrow du = C_v dT + \frac{a}{v^2} dv = f(T, v)$

Enthalpy, h

- $h = h(P,T) \rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP = C_p\, dT + \left(\frac{\partial h}{\partial P}\right)_T dP$
- $dh = Tds + dP = C_P\, dT - T\left(\frac{\partial v}{\partial T}\right)_P dP + vdP$ ($\hookleftarrow$ 2^{nd} Tds Eqn.)

$$\boxed{\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P}$$

$$\boxed{dh = c_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP}$$

- Ideal gas: $\left(\frac{\partial h}{\partial P}\right)_T = v - \frac{TR}{P} = 0 \longrightarrow h \neq f(P)$
  $\left(\frac{\partial h}{\partial P}\right)_T = 0 = \left(\frac{\partial h}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = -\frac{v}{P}\left(\frac{\partial h}{\partial v}\right)_T \rightarrow \left(\frac{\partial h}{\partial v}\right)_T = 0$
  $\left(\frac{\partial h}{\partial P}\right)_T = 0 \longrightarrow h \neq f(P):$ $\qquad$ $\left(\frac{\partial h}{\partial v}\right)_T = 0 \rightarrow h \neq f(v)$

$$\longrightarrow dh = C_P\, dT = f(T)$$

- van der Waals' gas: $\Rightarrow h = f(T,P)$

$C_P - C_v$

- $s = s(v,T) \rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$
  $\left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \hookleftarrow \left[\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T},\ \left(\frac{\partial s}{\partial v}\right)_T = \frac{C_v}{T}\right]$
  $\longrightarrow C_P - C_V = T\left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P$
- $f(x,y,x) = 0 \rightarrow \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z = -1$
  $\longrightarrow \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = 1 \longrightarrow \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v$

$$\boxed{C_P - C_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = -T\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2}$$

- For liquids & solids, $\left(\frac{\partial v}{\partial T}\right)_P \rightarrow 0 \Rightarrow C_P \approx C_v \approx C$
- $\left(\frac{\partial v}{\partial T}\right)_P^2$ is +ve & $\left(\frac{\partial P}{\partial v}\right)_T$ is -ve for all known substances, $C_P \geqslant C_v$
- as $T \rightarrow 0$, $C_p \rightarrow C_v$, at $T = 0$, $C_P = C_v$

- Isothermal compressibility, $k_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$
- Volume expansivity, $\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$

$$\boxed{C_P - C_v = -T\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2 = \frac{\beta^2}{k_T} vT}$$

- Ideal gas: $Pv = RT \longrightarrow k_T = \frac{1}{P},\ \ \beta = \frac{1}{T}$

$$\boxed{C_p - C_v = R}$$

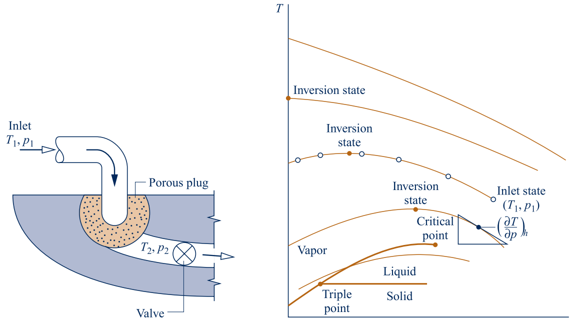
Clausius-Clapeyron Equation (for Phase Change)

- $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T = \frac{s_2 - s_1}{v_2 - v_1}$: phase change $\rightarrow T = T_{sat} =$ const.
- $\left(\frac{\partial P}{\partial T}\right)_v = \frac{dP}{dT}$, for mixture of 2 phases, $P = f(T)$
- $\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{h_2 - h_1}{T(v_2 - v_1)} \Rightarrow \boxed{\left.\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{Tv_{12}}}$ Clapeyron Eqn.

  Example: using only P-v-T data, estimate h_{fg} of R-134a at 20^{o}C
  - $v_{fg} = (v_g - v_f)_{sat,@20^o C} = 0.035153\ \mathrm{m}^3\ \mathrm{kg}$
  - $\left.\frac{dP}{dT}\right)_{sat,@20^o C} = \left.\frac{\Delta P}{\Delta T}\right)_{sat,@20^o C} = \frac{P_{sat,@24^o C} - P_{sat,@16^o C}}{24^0 C - 16^o C} = 17.70$ kPa/K
  - $h_{fg} = Tv_{fg} \left.\frac{dP}{dT}\right)_{sat,@20^o C} = (293.15)(0.035153)(17.70) = 182.40$ kJ/kg
    Tabulated value of h_{fg} @20^o C is 182.27 kJ/kg.
- $v_2 >> v_1 \rightarrow v_2 = \frac{RT}{P} \Rightarrow \boxed{\left.\frac{d\ln P}{d(1/T)}\right)_{sat} = -\frac{h_{fg}}{R}}$ Clausius-Clapeyron Eq.
  $\longrightarrow \ln\left(\frac{P_2}{P_1}\right)_{sat} = \frac{\Delta h}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- $\boxed{\ln P_{sat} = A + \frac{B}{T} + C\ln T + DT}$, widely used vapour-pressure Eq.

Gas Expansion & Joule-Thomson coefficient

The temperature behaviour of a fluid during a throttling process is described by Joule-Thomson coefficient, μ_{JT}.



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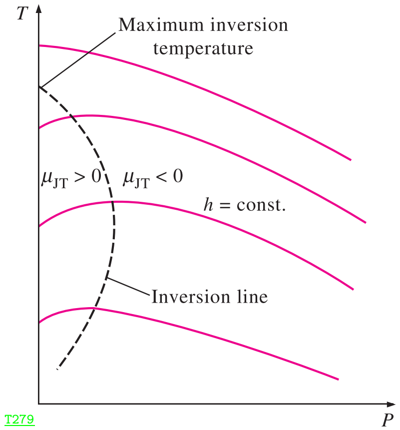
$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_h = \begin{cases} -ve & : \textit{temperature increase} \\ 0 & : \textit{temperature same} \\ +ve & : \textit{temperature drop} \end{cases}$$



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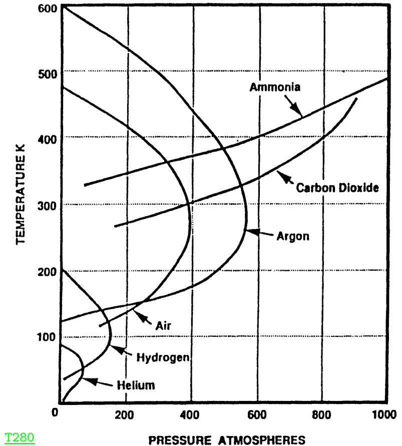

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A cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature. For hydrogen its value is -68°C and hydrogen must be cooled below this temperature if further cooling is to be achieved.