THE MOLLIER *h*-*s* DIAGRAM

Statement

Analyse the *h*-*s* (Mollier) diagram for a pure substance. In particular:

a) Demonstrate that isobars are straight lines in the two-phase region.

b) Compute the slope of the saturated vapour curve at low pressure and compare it with data from the Mollier diagram for water.

c) Compute the change in slope of isobars at each side of the saturated vapour curve.

d) Compute the change in slope of isotherms at each side of the saturated vapour curve.

e) How can specific-volume values be computed from isobars?

Se trata del análisis teórico del diagrama *h*-*s* de una sustancia pura. Se pide:

a) Demostrar que las isobaras son rectas en la región bifásica.

b) Calcular la pendiente de la línea de vapor saturado a bajas presiones y compararla con la del diagrama de Mollier del agua.

c) Calcular la variación de pendiente de las isobaras a un lado y otro de la curva de vapor saturado.

d) Calcular la variación de pendiente de las isotermas a un lado y otro de la curva de vapor saturado.

e) ¿Cómo se calculan volúmenes específicos a partir de las isobaras?

Solution.

a) Demonstrate that isobars are straight lines in the two-phase region.

From $\mathrm{d}h=T\mathrm{d}s+v\mathrm{d}p$ we deduce that the slope of isobars is:

$$\left.\frac{\mathrm{dh}}{\mathrm{d}s}\right|_p=T$$

But inside the two-phase region the isotherms coincide with the isobars because they are linked by Clapeyron equation, $p=p_v(T)$, given by:

$$\left.\frac{\mathrm{d}p}{\mathrm{d}T}\right|_{sat}=\frac{s_\mathrm{V}-s_\mathrm{L}}{v_\mathrm{V}-v_\mathrm{L}}=\frac{h_\mathrm{V}-h_\mathrm{L}}{T\left(v_\mathrm{V}-v_\mathrm{L}\right)}=\frac{h_\mathrm{LV}}{Tv_\mathrm{LV}}$$

thus, the slope of an isobar only depends on its pressure, that is kept constant.

b) Compute the slope of the saturated vapour curve at low pressure and compare it with data from the Mollier diagram for water.

From $\mathrm{d}h=T\mathrm{d}s+v\mathrm{d}p$ we deduce that $\partial h/\partial s|_\mathrm{sat}=T+v\partial p/\partial s|_\mathrm{sat}$, from $\mathrm{d}s=(c_p/T)\mathrm{d}T-\alpha v\mathrm{d}p$ we deduce that $\partial s/\partial p|_\mathrm{sat}=(c_p/T)\partial T/\partial p|_\mathrm{sat}-\alpha v$, and, with $\partial p/\partial T|_\mathrm{sat}=h_\mathrm{LV}/(Tv_\mathrm{LV})$ and the ideal gas approximation we get:

$$\left.\frac{\mathrm{d}h}{\mathrm{d}s}\right|_{sat}=T+\frac{v}{\left.\frac{\mathrm{d}s}{\mathrm{d}p}\right|_{sat}}=T+\frac{v}{\frac{c_p}{T}\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right|_{sat}-\alpha v}=T+\frac{v}{\frac{c_p}{T}\frac{Tv_\mathrm{LV}}{h_\mathrm{LV}}-\alpha v}=\frac{c_p\frac{Tv_\mathrm{LV}}{h_\mathrm{LV}}-T\alpha v+v}{\frac{c_p}{T}\frac{Tv_\mathrm{LV}}{h_\mathrm{LV}}-\alpha v}\overset{p\to 0}{=}\frac{c_pT^2}{c_pT-h_\mathrm{LV}}$$

With c_p=1900 J/(kg·K) and $h_{LV}=2.26\cdot10^6$ J/kg at T=373 K, we get $\partial h/\partial s|_{sat}=-170$ K, whereas by graphical computation from the Mollier diagram for water we get $\partial h/\partial s|_{sat}=-140000/1000=-140$ K, not too astray.

c) Compute the change in slope of isobars at each side of the saturated vapour curve.

It has been deduced that $\partial h/\partial s|_p=T$, thus, because isotherms are continuous (not their slopes), the slope of isobars are continuous when traversing the saturated line.

d) Compute the change in slope of isotherms at each side of the saturated vapour curve.

Similarly:

$$\left.\frac{\mathrm{d}h}{\mathrm{d}s}\right|_T = T + \frac{v}{\left.\frac{\mathrm{d}s}{\mathrm{d}p}\right|_T} = T + \frac{v}{-\alpha v} = T - \frac{1}{\alpha}$$

that can be deduced also from the general expressions of dh and ds in terms of T and p:

$$\left.\frac{\mathrm{d}h}{\mathrm{d}s}\right|_T = \left.\frac{c_p\mathrm{d}T + (1-\alpha T)v\mathrm{d}p}{\frac{c_p}{T}\mathrm{d}T - \alpha v\mathrm{d}p}\right|_T = \frac{(1-\alpha T)v}{-\alpha v} = T - \frac{1}{\alpha}$$

Since α is discontinuous (α=0 for ideal liquids, $\alpha=\infty$ for two-phase mixtures, $\alpha=1/T$ for ideal gases), the slope of the isotherms too. In fact, with the incompressible liquid model the slope becomes infinite, whereas with the ideal gas model the slope is zero.

e) How can specific-volume values be computed from isobars?

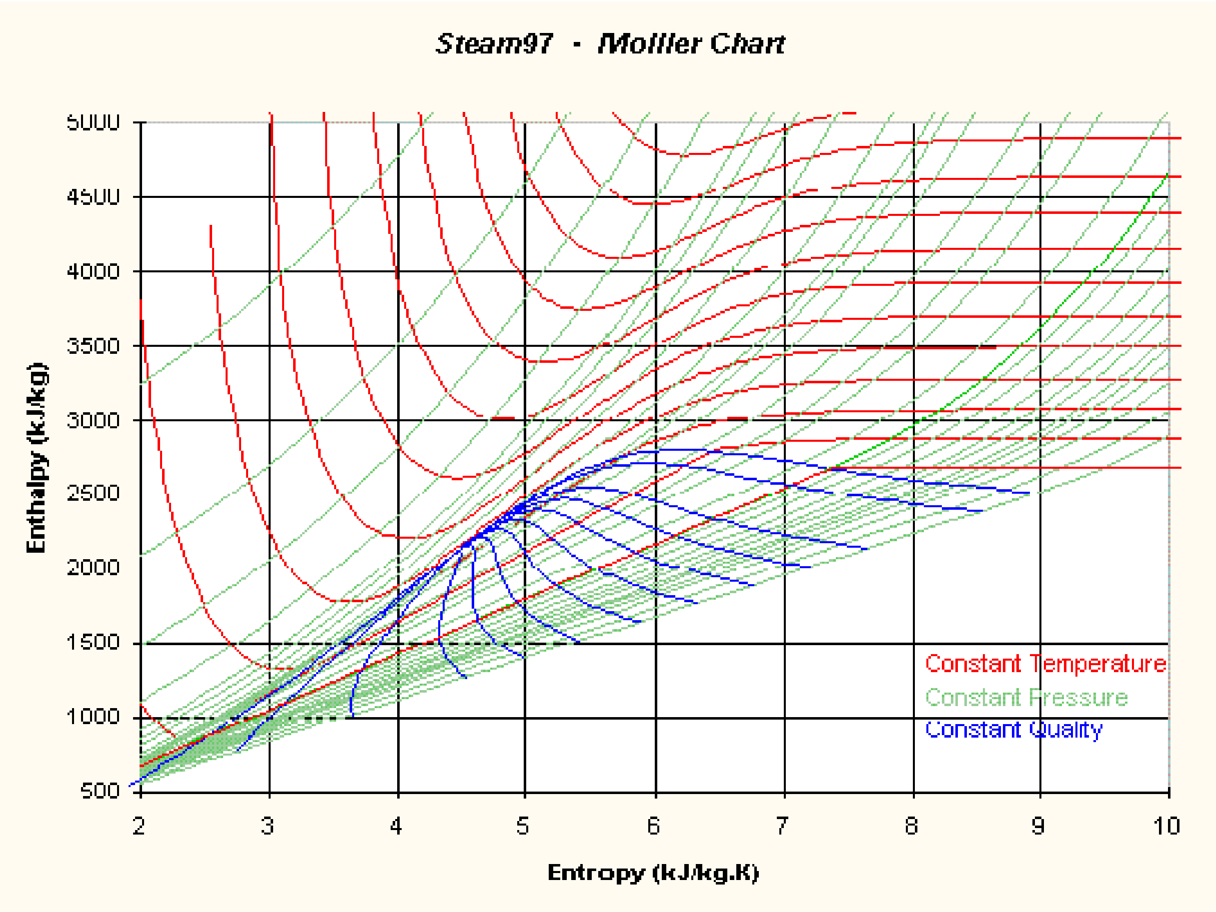
From dh=Tds+vdp we deduce that $v=\partial h/\partial p|_s$.

The slope of the isochors is:

$$\left.\frac{\mathrm{d}h}{\mathrm{d}s}\right|_v = T + \frac{v}{\left.\frac{\mathrm{d}s}{\mathrm{d}p}\right|_v} = T + \frac{v}{\frac{c_p}{T}\frac{\kappa}{\alpha} - \alpha v} = T + \frac{1}{\frac{\kappa c_v}{\alpha v T}} = T + \frac{\alpha v T}{\kappa c_v} \xrightarrow{\text{PGM}} \left.\frac{\mathrm{d}h}{\mathrm{d}s}\right|_v = \gamma T$$

Notice that with the ideal gas model, both, isobars and isochors, are exponential functions in the h-s diagram because their slope grows with T and h does, but isochors have a γ-times greater slope.

Comments. You may check the results with an actual h-s diagram as the following one. Notice that the perfect gas model (PGM) only applies to the right of the diagram (i.e. at low pressure).


Steam97 - Mollier Chart
Enthalpy (kJ/kg)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
2
3
4
5
6
7
8
9
10
Entropy (kJ/kg.K)
Constant Temperature
Constant Pressure
Constant Quality

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