Extrapolating Properties Into the Sub-Cooled Phase

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Originally dated June, 2018. The following was an accompanying document to my vapor compression refrigeration cycle simulation codes which I developed while I was a master's student at the University of New Hampshire in the laboratory of Prof. Chris White. In our case the evaluation of thermodynamic properties of subcooled coolant, R-134a, was not available from the proprietor's data. Therefore, the available data had to be extrapolated into the subcooled phase. This is accomplished by a simple exercise in differential thermodynamics. This document is merely an enumeration of evaluations solving for one thermodynamic property as a function of two others. This is all applicable assuming you have tabulations of the properties of the substance in question in the saturated liquid phase, including specific heat. I include this here as a free resource. It is easily transferable for anyone needing to develop quick and easy models of a pure subcooled substance as part of a subroutine of a larger model.

Contents

1 Introduction

We make use of a number of simple laws and assumptions to get these results, and try our best to quantify errors where appropriate. Essentially we take information about the substance in its saturated liquid state, employ differential thermodynamic relations, and integrate on a clever process to get an explicit formulation in the subcooled region. The results here are not a complete closure of the thermodynamic state-space. Table 1 should elucidate what is knowable in this framework and what is not.

$_{var2}\backslash^{var1}$	T	P	v	u	h	s
T	$*$	$\otimes$	$\otimes$			
P	$\otimes$	$*$		$\otimes$	$\otimes$	$\otimes$
v	$\otimes$		$*$	$\otimes$	$\otimes$	$\otimes$
u		$\otimes$	$\otimes$	$*$		
h		$\otimes$	$\otimes$		$*$	
s		$\otimes$	$\otimes$			$*$

Table 1: given an input state of two distinct properties, $\otimes$ indicates that all other properties are known explicitly, otherwise this is not the case

As is the standard axiom, if at least two thermodynamic properties are fixed, it defines a state, and all other properties are fixed in that state. In principle this means all thermal properties are functions of two other properties. We further remark that we assume the liquid is incompressible to make these calculations, and therefore v and P are coupled, and do not constitute independent properties, which makes them an invalid input pairing.

The bulk of the work is in the following section for temperature and pressure inputs. Subsequent sections rely on first deriving a way to get temperature and/or pressure, thereby reducing the calculation of the remaining state variables to an already solved problem.

2 Given Tempurature and Pressure

2.1 Evaluate volume

Firstly we begin with a hard assumption of incompressibility. When you have been given pressure, simply use the saturation value for specific volume ($v = \frac{1}{\rho}$).

$$v = v_f(P) + \epsilon_v \tag{1}$$

Where ϵ_v is an error term associated with our assumption of incompressibility. We will try our best not to forget about the epsilons as we go.

2.2 Evaluate enthalpy and energy

Given Temperature and Pressure it should be possible to easily evaluate u and h by integrating a constant pressure process. Simply begin at T_{sat} and integrate to T. The error associated with this calculation comes from the assumption that the heat capacity is constant with respect to temperature. To factor this in, lets merely use the first term of the Taylor series appx. and let the error be a linear function of temperature.

$$c_p(T,P) = c_p(T_{sat},P) + a_1(T_{sat},P) * (T - T_{sat}) + a_2(T_{sat},P) * (T - T_{sat})^2 + ...$$

then recast with an epsilon and drop the higher order terms

$$c_p(T,P) = c_p(P) + \epsilon_c(T - T_{sat}) + O\big((T - T_{sat})^2\big)$$

$$h = h_f(P) + \int_{T_{sat}(P)}^{T} \big[c_p(P) + \epsilon_c(T - T_{sat}(P))\big]dT \tag{2}$$

The constants are shown with explicit dependence on pressure merely as a reminder that you do still need two properties to determine the state.

$$h = h_f(P) + c_p(P)(T - T_{sat}(P)) + \frac{\epsilon_c}{2}(T - T_{sat}(P))^2 \tag{3}$$

This approximation is fine if ϵ_c is truly small; it depends on what you're calculating and what you consider "close enough".

Now to capture the internal energy u, we need only look to our assumption of incompressibility when we integrate the differential expression defining enthalpy on a constant pressure process (this way, the term vdP integrates to zero).

$$\Delta u = \Delta h - P\Delta v \tag{4}$$

due to incompressibility this becomes

$$\Delta u = \Delta h - P\epsilon_v$$

So we do have error scaling linearly with pressure in addition to the error associated with ΔT. but for subcooled liquids $\Delta u = \Delta h$ is almost always assumed no matter what; therefore, we discard it. Here's the full explicit formulation with the relevant error terms included.

$$u = u_f(P) + c_p(P)(T - T_{sat}) + \frac{\epsilon_c}{2}(T - T_{sat})^2 - P\epsilon_v \tag{5}$$

All of this assuming you have a functional relationship for $c_p(P)$. If, like me, you like to live on the edge and only have one value for the heat capacity for all cases then you are essentially letting god decide the outcome behind your back, since specific heat capacity can sometimes vary strongly with temperature and pressure.

2.3 Evaluate Entropy

now we must achieve an expression for entropy. We simply integrate the second law of thermodynamics on a reversible constant pressure process.

$$\Delta s = \int \frac{\delta q}{T}$$

We know that a heat transfer process over a zero temperature difference is completely reversible, so assign the temperature in the denominator to be the current temperature of the substance. Now, since the process is also constant pressure we know $\delta q = dh$ so introduce the relationship we derived from the previous section and differentiate it.

$$dh = c_p(P)dT + \epsilon_c(T - T_{sat})dT$$

We arrive at the following.

$$s - s_f(P) = \int_{T_{sat}(P)}^{T} \frac{c_p(P)dt}{t} + \int_{T_{sat}(P)}^{T} \frac{\epsilon_c(t - T_{sat}(P))dt}{t} \tag{6}$$

integrate to find

$$s = s_f(P) + c_p(P)\log\left(\frac{T}{T_{sat}(P)}\right) + \epsilon_c(T - T_{sat}(P)) + \epsilon_c T_{sat}(P)\log\left(\frac{T}{T_{sat}(P)}\right) \tag{7}$$

With two error terms scaling linearly with ΔT and $T_{sat}\log\left(\frac{T}{T_{sat}(P)}\right)$ respectively

3 Given Temperature and Specific Volume

This is easy. Use the incompressibility assumption

$$v = v_f + \epsilon_v$$

and then use the saturated tables to get pressure.

$$P = f(v_f) + \epsilon_P$$

We now have temperature and pressure. Simply follow the previous section to get any property.

4 Given Pressure and a ”py”-suffixed property

For brevity we say ”’py’-suffixed property” for either energy, enthalpy, or entropy (Yes, I know you don’t say ”Enerpy”). It is natural to lump these into one section, as the methods for dealing with them are quite similar.

It would be easy enough to simply invert the relationships from the section on temperature and pressure (section 2). There are, however, some faster tricks. The following section will be more terse than the previous, since by now you seem to be catching on to the process.

4.1 Evaluate Specific Volume

As before, regardless of what property is supplied alongside pressure, the specific volume is immediately available due to our assumption of incompressibility.

$$v = v_f(P) + \epsilon_v$$

4.2 Evaluate Temperature

No bones about it, simply invert the relationships derived in section 2. For completeness the explicit formulations are given here

when u is given (c_p may be used for u calculations because of incompressibility)

$$T = T_{sat} + \frac{u - u_f(P)}{c_p(P)} \tag{8}$$

when h is given, it is straightforward

$$T = T_{sat} + \frac{h - h_f(P)}{c_p(P)} \tag{9}$$

when s is given (Remember, these must be done in Kelvin)

$$T = T_{sat} \exp\left(\frac{s - s_f(P)}{c_p(P)}\right) \tag{10}$$

4.3 Converting Energy to Enthalpy

Given energy or enthalpy, you may easily get one from the other. v is immediately available via incompressibility. then simply use the definition of enthalpy.

$$u = h - Pv + P\epsilon_v \tag{11}$$

$$h = u + Pv + P\epsilon_v \tag{12}$$

Errors here scale linearly with pressure.

4.4 Evaluate Entropy given either Enthalpy or Energy

This is induced from the $s(T)$ and $T(h)$ relations in the previous sections. We may express the temperature as either

$$T = T_{sat} + \frac{1}{c_p(P)}(u - u_f)$$

or

$$T = T_{sat} + \frac{1}{c_p(P)}(h - h_f)$$

Then entropy is given explicitly as follows.

$$s = c_p(P) \log \left(\frac{\frac{1}{c_p(P)}(u - u_f) + T_{sat}}{T_{sat}} \right) + s_f \tag{13}$$

$$s = c_p(P) \log \left(\frac{\frac{1}{c_p(P)}(h - h_f) + T_{sat}}{T_{sat}} \right) + s_f \tag{14}$$

5 Appendix

5.1 A note on the exclusion of the case where temperature and "py"-suffixed properties are the givens

If one took temperature and either energy, enthalpy, or entropy you could attempt to invert the relationships in section 2 to find pressure, but there are complications due to the unspecified specific heat function. These formulations are not explicit, and given that $c_p(P)$ and $T_{sat}(P)$ are determined by table-lookup, and may be treated programmatically as nonlinear functions, some kind of numerical solver would be employed to squeeze out a pressure value.

Therefore, in the interest of keeping this article "easy to use" we exclude these cases and leave them as an exercise for the reader.

5.2 Specific Heats of Saturated Liquids

T_{sat} $[K]$	P_{sat} $[kPa]$	c_p $\left[\frac{kJ}{kgK}\right]$
230	42.25	1.249
240	72.73	1.267
250	115.7	1.287
260	176.8	1.308
270	260.5	1.333
280	372.9	1.361
290	518.6	1.393
300	703.1	1.432
310	933.7	1.481
320	1217	1.543
330	1560	1.627
340	1972	1.751
350	2462	1.961
360	3042	2.437
370	3743	5.105

Table 2: Specific Heats of Saturated Liquid R-134a. src: Incropera "Fundamentals of Heat and Mass Transfer"