

# Analysis of Enthalpy Approximation for Compressed Liquid Water

Milivoje M. Kostic

e-mail: kostic@niu.edu  
Northern Illinois University,  
DeKalb, IL 60115-2854

*It is custom to approximate solid and liquid thermodynamic properties as being a function of temperature only, since they are virtually incompressible, and  $Pdv$  boundary work may be neglected. Furthermore, in classical literature, for isothermal compression processes, a general "improvement" and correction for liquid enthalpy approximation is given by adding the "pressure correction,"  $v dP$ , to the corresponding saturation value. It is shown that such correction given for isothermal processes is generally valid for isentropic processes only. Analysis of water real properties, over the saturation temperature range and a wide pressure range up to 100 MPa, shows that the recommended corrections are only beneficial for higher pressures at smaller temperatures (below 200°C), insignificant for smaller pressures at most of the temperatures, about the same but opposite sign (thus unnecessary) for intermediate temperatures and pressures, and more erroneous (thus counterproductive and misleading) for higher temperatures and pressures, than the corresponding saturation values without any correction. The misconception in the literature is a result of the erroneous assumption, that due to incompressibility for liquids in general, the internal energy is less dependent on pressure than enthalpy. [DOI: 10.1115/1.2175090]*

*Keywords: enthalpy, water, thermodynamic properties, thermodynamic analysis, isothermal, isentropic*

## 1 Introduction

Since solids and liquids are virtually (but not exactly) incompressible, then the compression work,  $Pdv$ , could be neglected and thus many properties virtually will not be a function of pressure but temperature only, such as specific internal energy,  $u$ , etc. Furthermore, any process is also at the same time an isochoric, constant-volume process. Namely, the isobaric, constant-pressure process will be a simultaneously constant-volume process for an incompressible substance, so that specific heat at constant pressure,  $c_p$ , and constant volume,  $c_v$ , are the same, or approximately the same for virtually incompressible real solids and liquids, particularly when compared to vapors and gases, i.e.:

$$u \approx u(T) \approx u_{\text{sat}}(T) \text{ and } c_p \approx c_v \approx c(T) \quad (1)$$

Even the specific enthalpy for a liquid (from here on word "specific" will be assumed and omitted for brevity), can be approximated to be independent from pressure and conveniently taken to be equal to the corresponding saturated liquid value at the given temperature:

$$h(P, T) \approx h(T) \approx h_{\text{sat}}(T) \quad (2)$$

However, enthalpy is unique, since it is explicitly defined as a function of pressure, namely:

$$h \equiv u + P \cdot v \quad \text{thus,} \quad h(T, P) = u(T, P) + P \cdot v \approx u_{\text{sat}}(T) + P \cdot v \quad (3)$$

Therefore, it is common in most engineering references, including classical and widely used thermodynamics textbooks [1,2], to evaluate the change of enthalpy, assuming incompressibility ( $dv=0$ ), but taking correction for pressure increase as:

$$\begin{aligned} dh &= d(u + P \cdot v) = \underbrace{du}_{dh_{du}} + \underbrace{P \cdot dv}_{dh_{dv}} + \underbrace{v \cdot dP}_{dh_{dP}} \Big|_{dv=0} \approx du + v dP \\ &\approx cdT + \underbrace{v dP}_{dh_{dP} \approx dh_{\text{corr}}} \end{aligned} \quad (4)$$

Furthermore, for isothermal processes ( $dT=0$  and  $du \approx 0$ ), then  $dh \approx v dP$ , and finally, for finite pressure difference change from saturated pressure,  $P_{\text{sat}}$ , corresponding to the given temperature,  $T$ , the specific enthalpy with correction,  $h_{\text{corr}}(T, P)$  at that temperature,  $T$ , and any pressure,  $P$ , will be [1,2]:

$$\Delta h_{\text{corr}} = h_{\text{corr}}(P, T) - h_{\text{sat}}(T) = v_{\text{sat}}(T) \cdot \overbrace{(P - P_{\text{sat}})}^{\Delta P_{\text{sat}}} \quad (5a)$$

$$h_{\text{corr}}(P, T) = h_{\text{sat}}(T) + \underbrace{v_{\text{sat}}(T) \cdot (P - P_{\text{sat}})}_{\Delta h_{\text{corr}}} \quad (5b)$$

where,  $h_{\text{sat}}(T)$  and  $v_{\text{sat}}(T)$  are liquid saturation enthalpy and liquid saturation specific volume at given temperature,  $T$ , respectively. It is stated in many references, including [1,2], that the above equations (5a) and (5b) are recommended as the correction for isothermal, liquid enthalpy dependence on pressure, and that it is more accurate than a simple, approximation without correction,  $h_{\text{sat}}$  (Eq. (2)).

It is the objective of this paper to point out the erroneous general recommendations in the literature. The correction (Eq. (5)), as recommended in many references, is only useful for higher pressures at smaller temperatures, but is actually more erroneous (thus counterproductive and misleading) for higher temperatures and pressures, and is about the same (but opposite sign, thus not necessary) for intermediate temperatures, than the simple approximation (Eq. (2)) without any correction. Corresponding analysis using real water data [3] and physical justification are presented below.

Contributed by the Heat Transfer Division of ASME for publication in the JOURNAL OF HEAT TRANSFER. Manuscript received December 13, 2004; final manuscript received November 1, 2005. Review conducted by John H. Lienhard V. Paper presented at the 2004 ASME International Mechanical Engineering Congress (IMECE2004), November 13–19, 2004, Anaheim, California, USA.

Table 1 Compressed liquid water property data at 260 °C [3] and different enthalpy corrections

$P$ (MPa)	$v$ (m <sup>3</sup> /kg)	$u$ (kJ/kg)	$h$ (kJ/kg)	$s$ (kJ/kg K)	$C_v$ (kJ/kg K)	$C_p$ (kJ/kg K)	$c_{\text{sound}}$ (m/s)	$\mu_{JT}$ (K/MPa)	$\Delta h_{\Delta\mu}$ (kJ/kg)	$\Delta h_{\Delta v}$ (kJ/kg)	$\Delta h_{\Delta P}$ (kJ/kg)	$\Delta h_{\text{corr}}$ (kJ/kg)	$\Delta h$ or $-\int \mu C_p dP$ (kJ/kg)	$h_{\text{sat}}-h$ (kJ/kg)	$h_{\text{corr}}-h$ (kJ/kg)
4.69sat	0.001276	1129.0	1135.0	2.8849	3.1301	4.9856	1105.3	0.03472	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.001276	1128.5	1134.9	2.8841	3.1299	4.9804	1107.2	0.03373	-0.50	0.00	0.39	0.39	-0.05	0.10	0.49
10	0.001265	1121.6	1134.3	2.8710	3.1257	4.9019	1135.8	0.01884	-7.40	-0.08	6.74	6.77	-0.70	0.70	7.47
15	0.001256	1115.1	1134.0	2.8586	3.1220	4.8336	1162.6	0.00582	-13.90	-0.20	13.05	13.15	-1.00	1.00	14.15
20	0.001247	1109.0	1134.0	2.8469	3.1187	4.7733	1187.8	-0.00568	-20.00	-0.35	19.31	19.53	-1.00	1.00	20.53
25	0.001239	1103.2	1134.2	2.8357	3.1158	4.7195	1211.7	-0.01595	-25.80	-0.53	25.52	25.91	-0.75	0.80	26.71
30	0.001231	1097.8	1134.7	2.8250	3.1131	4.6711	1234.3	-0.02519	-31.20	-0.74	31.70	32.30	-0.26	0.30	32.60
35	0.001224	1092.5	1135.4	2.8148	3.1107	4.6272	1256.0	-0.03355	-36.50	-0.98	37.84	38.68	0.42	-0.40	38.28
40	0.001217	1087.6	1136.3	2.8050	3.1084	4.5871	1276.7	-0.04117	-41.40	-1.24	43.94	45.06	1.28	-1.30	43.76
45	0.001211	1082.8	1137.3	2.7955	3.1063	4.5502	1296.6	-0.04816	-46.20	-1.52	50.01	51.44	2.30	-2.30	49.14
50	0.001204	1078.2	1138.4	2.7864	3.1043	4.5162	1315.8	-0.05458	-50.80	-1.82	56.05	57.82	3.46	-3.40	54.42
55	0.001199	1073.8	1139.7	2.7775	3.1024	4.4847	1334.3	-0.06051	-55.20	-2.12	62.05	64.20	4.76	-4.70	59.50
60	0.001193	1069.6	1141.1	2.7690	3.1006	4.4553	1352.2	-0.06601	-59.40	-2.45	68.03	70.58	6.17	-6.10	64.48
65	0.001187	1065.5	1142.7	2.7607	3.0989	4.4279	1369.5	-0.07113	-63.50	-2.80	73.98	76.96	7.70	-7.70	69.26
70	0.001182	1061.6	1144.3	2.7526	3.0973	4.4022	1386.3	-0.07590	-67.40	-3.15	79.91	83.34	9.32	-9.30	74.04
75	0.001177	1057.7	1146.0	2.7447	3.0957	4.3781	1402.6	-0.08037	-71.30	-3.52	85.80	89.72	11.03	-11.00	78.72
80	0.001172	1054.0	1147.8	2.7371	3.0943	4.3553	1418.5	-0.08456	-75.00	-3.90	91.68	96.10	12.83	-12.80	83.30
85	0.001167	1050.5	1149.7	2.7297	3.0928	4.3338	1433.9	-0.08850	-78.50	-4.29	97.53	102.48	14.71	-14.70	87.78
90	0.001163	1047.0	1151.6	2.7224	3.0914	4.3134	1449.0	-0.09220	-82.00	-4.69	103.35	108.86	16.67	-16.60	92.26
95	0.001158	1043.6	1153.7	2.7153	3.0901	4.2940	1463.7	-0.09570	-85.40	-5.09	109.15	115.24	18.69	-18.70	96.54
100	0.001154	1040.3	1155.8	2.7084	3.0888	4.2756	1478.1	-0.09901	-88.70	-5.51	114.93	121.62	20.77	-20.80	100.82

Table 2 Compressed liquid water property data at different temperatures and pressures [3]

<i>P</i> (MPa)	<i>T</i> =4 °C			<i>T</i> =20 °C			<i>T</i> =50 °C			<i>T</i> =100 °C			<i>T</i> =150 °C		
	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)
Sat	0.001000	16.81	16.81	0.001002	83.912	83.914	0.001012	209.33	209.34	0.001044	419.06	419.17	0.001091	631.66	632.18
5	0.000998	16.81	21.80	0.001000	83.609	88.607	0.001010	208.59	213.64	0.001041	417.64	422.85	0.001088	629.55	634.98
10	0.000995	16.79	26.75	0.000997	83.308	93.281	0.001008	207.86	217.94	0.001039	416.23	426.62	0.001084	627.27	638.11
15	0.000993	16.77	31.66	0.000995	83.007	97.934	0.001006	207.15	222.23	0.001036	414.85	430.39	0.001081	625.05	641.27
20	0.000990	16.74	36.55	0.000993	82.708	102.57	0.001004	206.44	226.51	0.001034	413.50	434.17	0.001078	622.89	644.45
25	0.000988	16.70	41.40	0.000991	82.409	107.18	0.001001	205.75	230.79	0.001031	412.17	437.95	0.001075	620.78	647.66
30	0.000986	16.65	46.23	0.000989	82.112	111.77	0.000999	205.07	235.05	0.001029	410.87	441.74	0.001072	618.73	650.89
35	0.000984	16.59	51.02	0.000987	81.815	116.34	0.000997	204.40	239.31	0.001027	409.60	445.54	0.001069	616.72	654.14
40	0.000981	16.53	55.79	0.000985	81.520	120.90	0.000995	203.75	243.56	0.001025	408.35	449.33	0.001066	614.77	657.42
45	0.000979	16.46	60.53	0.000982	81.225	125.44	0.000993	203.10	247.80	0.001022	407.13	453.14	0.001064	612.85	660.71
50	0.000977	16.38	65.24	0.000980	80.931	129.95	0.000991	202.46	252.03	0.001020	405.93	456.94	0.001061	610.98	664.02
55	0.000975	16.30	69.93	0.000978	80.637	134.45	0.000989	201.84	256.26	0.001018	404.76	460.75	0.001058	609.15	667.35
60	0.000973	16.21	74.59	0.000977	80.345	138.94	0.000988	201.22	260.47	0.001016	403.61	464.56	0.001056	607.36	670.69
65	0.000971	16.12	79.23	0.000975	80.053	143.40	0.000986	200.61	264.68	0.001014	402.47	468.37	0.001053	605.61	674.05
70	0.000969	16.01	83.84	0.000973	79.762	147.85	0.000984	200.01	268.88	0.001012	401.36	472.19	0.001051	603.89	677.43
75	0.000967	15.91	88.43	0.000971	79.471	152.29	0.000982	199.42	273.07	0.001010	400.27	476.00	0.001048	602.21	680.81
80	0.000965	15.80	93.00	0.000969	79.182	156.70	0.000980	198.84	277.26	0.001008	399.20	479.82	0.001046	600.56	684.21
85	0.000963	15.68	97.55	0.000967	78.893	161.10	0.000978	198.26	281.44	0.001006	398.14	483.64	0.001043	598.95	687.63
90	0.000961	15.56	102.07	0.000965	78.604	165.49	0.000977	197.70	285.61	0.001004	397.11	487.46	0.001041	597.36	691.05
95	0.000959	15.44	106.58	0.000964	78.317	169.86	0.000975	197.14	289.77	0.001002	396.09	491.29	0.001039	595.81	694.48
100	0.000958	15.31	111.06	0.000962	78.031	174.22	0.000973	196.59	293.92	0.001000	395.09	495.11	0.001036	594.29	697.93

<i>P</i> (MPa)	<i>T</i> =200 °C			<i>T</i> =250 °C			<i>T</i> =300 °C			<i>T</i> =350 °C		
	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)	<i>v</i> (m <sup>3</sup> /kg)	<i>u</i> (kJ/kg)	<i>h</i> (kJ/kg)
Sat	0.001157	850.47	852.27	0.001252	1080.8	1085.8	0.001404	1332.9	1345.0	0.00174	1642.1	1670.9
5	0.001153	847.91	853.68	0.00125	1079.5	1085.7	<i>P</i> <sub>sat</sub> =8.5879 MPa			<i>P</i> <sub>sat</sub> =16.529 MPa		
10	0.001148	844.31	855.80	0.001241	1073.4	1085.8	0.001398	1329.4	1343.3			
15	0.001144	840.84	857.99	0.001233	1067.6	1086.1	0.001378	1317.6	1338.3			
20	0.001139	837.49	860.27	0.001225	1062.2	1086.7	0.001361	1307.1	1334.4	0.001665	1612.7	1646.0
25	0.001135	834.24	862.61	0.001218	1057.0	1087.4	0.001346	1297.6	1331.3	0.001599	1583.9	1623.9
30	0.00113	831.10	865.02	0.001211	1052.0	1088.4	0.001332	1288.9	1328.9	0.001553	1562.2	1608.8
35	0.001126	828.06	867.48	0.001205	1047.3	1089.4	0.001320	1280.8	1327.0	0.001517	1544.5	1597.6
40	0.001122	825.10	870.00	0.001199	1042.7	1090.7	0.001308	1273.3	1325.6	0.001488	1529.3	1588.8
45	0.001119	822.23	872.57	0.001193	1038.4	1092.0	0.001298	1266.2	1324.6	0.001464	1515.9	1581.8
50	0.001115	819.45	875.19	0.001187	1034.2	1093.5	0.001288	1259.6	1324.0	0.001443	1503.9	1576.1
55	0.001111	816.73	877.85	0.001182	1030.1	1095.1	0.001279	1253.3	1323.6	0.001424	1493.1	1571.4
60	0.001108	814.09	880.55	0.001176	1026.2	1096.8	0.001270	1247.3	1323.5	0.001407	1483.1	1567.5
65	0.001104	811.51	883.29	0.001171	1022.5	1098.6	0.001262	1241.6	1323.6	0.001391	1473.8	1564.3
70	0.001101	809.00	886.07	0.001167	1018.8	1100.5	0.001254	1236.1	1323.9	0.001377	1465.2	1561.6
75	0.001098	806.56	888.89	0.001162	1015.3	1102.4	0.001247	1230.9	1324.4	0.001364	1457.1	1559.5
80	0.001095	804.17	891.73	0.001157	1011.8	1104.4	0.001240	1225.9	1325.1	0.001353	1449.5	1557.7
85	0.001091	801.83	894.61	0.001153	1008.5	1106.5	0.001233	1221.1	1325.9	0.001341	1442.3	1556.3
90	0.001088	799.55	897.51	0.001149	1005.3	1108.7	0.001227	1216.4	1326.8	0.001331	1435.5	1555.3
95	0.001086	797.32	900.44	0.001145	1002.1	1110.9	0.001221	1212.0	1327.9	0.001321	1429.0	1554.5
100	0.001083	795.14	903.40	0.001141	999.06	1113.1	0.001215	1207.6	1329.1	0.001312	1422.8	1554.0

**Table 3 Compressed liquid water enthalpies,  $h$ , their approximation differences,  $h_{sat}-h$  (Eq. (2)), and  $h_{corr}-h$  (Eq. (5)), and related percentages (Note: More erroneous approximations are indicated in bold.)**

$T^{\circ}\text{C} \rightarrow$	4°C		20°C		50°C		100°C		150°C		200°C		250°C		300°C		350°C	
	$h$ (kJ/kg)	$h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)
$P$ (MPa)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)	$h_{sat}-h$ (kJ/kg)	$h_{corr}-h$ (kJ/kg)
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Sat.	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>	<b>0%</b>
5	21.80	88.61	213.64	422.85	634.98	853.68	1085.70	Vapor										
	-4.98	0.02	-4.69	0.31	-4.30	0.75	-3.68	1.43	-2.80	2.13	-1.41	2.57	0.10	1.38				
	<b>-22.9%</b>	0.1%	<b>-5.3%</b>	0.4%	<b>-2.0%</b>	0.4%	<b>-0.9%</b>	0.3%	<b>-0.4%</b>	0.3%	<b>-0.2%</b>	<b>0.3%</b>	0.0%	<b>0.1%</b>				
10	26.75	93.28	217.94	426.62	638.11	855.80	1085.80	1343.30	Vapor									
	-9.93	0.07	-9.37	0.65	-8.60	1.51	-7.45	2.88	-5.93	4.46	-3.53	6.24	0.00	7.54	1.70	3.68		
	<b>-37.1%</b>	0.3%	<b>-10.0%</b>	0.7%	<b>-3.9%</b>	0.7%	<b>-1.7%</b>	0.7%	<b>-0.9%</b>	0.7%	-0.4%	<b>0.7%</b>	0.0%	<b>0.7%</b>	0.1%	0.3%		
15	31.66	97.93	222.23	430.39	641.27	857.99	1086.10	1338.30	Vapor									
	-14.85	0.15	-14.02	1.00	-12.89	2.28	-11.22	4.33	-9.09	6.75	-5.72	9.83	-0.30	13.50	6.70	15.70		
	<b>-46.9%</b>	0.5%	<b>-14.3%</b>	1.0%	<b>-5.8%</b>	1.0%	<b>-2.6%</b>	1.0%	<b>-1.4%</b>	1.1%	-0.7%	<b>1.1%</b>	0.0%	<b>1.2%</b>	0.5%	<b>1.2%</b>		
20	36.55	102.57	226.51	434.17	644.45	860.27	1086.70	1334.40	1646.00									
	-19.74	0.27	-18.66	1.38	-17.17	3.06	-15.00	5.76	-12.27	9.02	-8.00	13.33	-0.90	19.16	10.60	26.62	24.90	30.94
	<b>-54.0%</b>	0.7%	<b>-18.2%</b>	1.3%	<b>-7.6%</b>	1.4%	<b>-3.5%</b>	1.3%	<b>-1.9%</b>	1.4%	-0.9%	<b>1.5%</b>	-0.1%	<b>1.8%</b>	0.8%	<b>2.0%</b>	1.5%	<b>1.9%</b>
30	46.23	111.77	235.05	441.74	650.89	865.02	1088.40	1328.90	1608.80									
	-29.41	0.59	-27.86	2.20	-25.71	4.64	-22.57	8.63	-18.71	13.49	-12.75	20.15	-2.60	29.97	16.10	46.17	62.10	85.54
	<b>-63.6%</b>	1.3%	<b>-24.9%</b>	2.0%	<b>-10.9%</b>	2.0%	<b>-5.1%</b>	2.0%	<b>-2.9%</b>	2.1%	-1.5%	<b>2.3%</b>	-0.2%	<b>2.8%</b>	1.2%	3.5%	3.9%	<b>5.3%</b>
40	55.79	120.90	243.56	449.33	657.42	870.00	1090.70	1325.60	1588.80									
	-38.98	1.03	-36.99	3.08	-34.22	6.25	-30.16	11.47	-25.24	17.86	-17.73	26.73	-4.90	40.19	19.40	63.51	82.10	122.94
	<b>-69.9%</b>	1.8%	<b>-30.6%</b>	2.6%	<b>-14.0%</b>	2.6%	<b>-6.7%</b>	2.6%	<b>-3.8%</b>	2.7%	-2.0%	<b>3.1%</b>	-0.4%	<b>3.7%</b>	1.5%	<b>4.8%</b>	5.2%	<b>7.7%</b>
50	65.24	129.95	252.03	456.94	664.02	875.19	1093.50	1324.00	1576.10									
	-48.43	1.58	-46.04	4.05	-42.69	7.90	-37.77	14.30	-31.84	22.17	-22.92	33.11	-7.70	49.91	21.00	79.15	94.80	153.04
	<b>-74.2%</b>	2.4%	<b>-35.4%</b>	3.1%	<b>-16.9%</b>	3.1%	<b>-8.3%</b>	3.1%	<b>-4.8%</b>	3.3%	-2.6%	<b>3.8%</b>	-0.7%	<b>4.6%</b>	1.6%	<b>6.0%</b>	6.0%	<b>9.7%</b>
60	74.59	138.94	260.47	464.56	670.69	880.55	1096.80	1323.50	1567.50									
	-57.78	2.23	-55.03	5.08	-51.13	9.58	-45.39	17.11	-38.51	26.40	-28.28	39.31	-11.00	59.12	21.50	93.69	103.40	179.04
	<b>-77.5%</b>	3.0%	<b>-39.6%</b>	3.7%	<b>-19.6%</b>	3.7%	<b>-9.8%</b>	3.7%	<b>-5.7%</b>	3.9%	-3.2%	<b>4.5%</b>	-1.0%	<b>5.4%</b>	1.6%	<b>7.1%</b>	6.6%	<b>11.4%</b>
80	93.00	156.70	277.26	479.82	684.21	891.73	1104.40	1325.10	1557.70									
	-76.19	3.82	-72.79	7.36	-67.92	13.04	-60.65	22.72	-52.03	34.69	-39.46	51.26	-18.60	76.56	19.90	120.18	113.20	223.64
	<b>-81.9%</b>	4.1%	<b>-46.4%</b>	4.7%	<b>-24.5%</b>	4.7%	<b>-12.6%</b>	4.7%	<b>-7.6%</b>	5.1%	-4.4%	<b>5.7%</b>	-1.7%	<b>6.9%</b>	1.5%	<b>9.1%</b>	7.3%	<b>14.4%</b>
100	111.06	174.22	293.92	495.11	697.93	903.40	1113.10	1329.10	1554.00									
	-94.25	5.76	-90.31	9.87	-84.58	16.62	-75.94	28.30	-65.75	42.78	-51.13	62.72	-27.30	92.89	15.90	144.26	116.90	262.14
	<b>-84.9%</b>	5.2%	<b>-51.8%</b>	5.7%	<b>-28.8%</b>	5.7%	<b>-15.3%</b>	5.7%	<b>-9.4%</b>	6.1%	-5.7%	<b>6.9%</b>	-2.5%	<b>8.3%</b>	1.2%	<b>10.9%</b>	7.5%	<b>16.9%</b>

## 2 Analysis

Compressed liquid water properties [3], for different pressure at 260°C, are presented in Table 1 and selected properties for different temperatures in Table 2. In addition, the corresponding corrections ( $\Delta h_{\Delta u}$ ,  $\Delta h_{\Delta v}$ , and  $\Delta h_{\Delta P}$ , see Eqs. (4)–(8)) are tabulated along with differences of the approximated enthalpies, without ( $h_{\text{sat}} - h$ ) and with correction ( $h_{\text{corr}} - h$ ) from the real enthalpy values,  $h$ , in the last two columns in Table 1, respectively, for saturated liquid water and compressed liquid water up to 100 MPa. Cumulative water enthalpy data with the corresponding differences and related percentages are presented in Table 3 for a wide range of temperatures between triple and critical points, and, a wide range of pressures from saturation up to 100 MPa. Note that the tabulated enthalpy differences with correction is based on Eq. (5), i.e., using correction  $\Delta h_{\text{corr}} \approx \Delta h_{\Delta P}$  only, as generally recommended in the literature, while corrections  $\Delta h_{\Delta u}$ , and  $\Delta h_{\Delta v}$  are neglected [1,2].

The corrections in Tables 1 and 3 are calculated using the following equations:

$$\Delta h_{\Delta u} = \Delta u = u(P, T) - u_{\text{sat}}(T) \quad (6)$$

$$\Delta h_{\Delta v} = \int P \cdot dv \cong \sum_{i=1}^{N-1} \left[ \frac{1}{2}(P_i + P_{i+1}) \right] \cdot (v_{i+1} - v_i) \quad (7)$$

$$\Delta h_{\Delta P} = \int v \cdot dP \cong \sum_{i=1}^{N-1} \left[ \frac{1}{2}(v_i + v_{i+1}) \right] \cdot (P_{i+1} - P_i) \approx \Delta h_{\text{corr}} \quad (8)$$

Note that in Eq. (5) the fluid is assumed to be incompressible, while in Eqs. (6)–(8) variability in  $v$ , although small, is taken into account, thus the differences in  $\Delta h_{\text{corr}}$  and  $\Delta h_{\Delta P}$  values in Table 1. Furthermore, for the isothermal compression, the correction  $\Delta h_{\Delta v}$  is much smaller than the corrections  $\Delta h_{\Delta u}$  and  $\Delta h_{\Delta P}$ , and thus it may be neglected. However, corrections  $\Delta h_{\Delta u}$  (negative) and corrections  $\Delta h_{\Delta P}$  (positive) are comparable in magnitude but opposite in sign, so it is better not to take the corrections, as in Eq. (2), than to take only the correction  $\Delta h_{\text{corr}} \approx \Delta h_{\Delta P}$ , as in Eq. (5). It will be shown below that the recommended enthalpy correction for the isothermal compression [1,2], is actually valid for isentropic compression.

It appears from real data values in Tables 1 and 2 that the magnitude of the negative correction  $\Delta h_{\Delta u}$  (i.e.,  $\Delta u$ ) increases with both pressure and temperature, while positive correction  $\Delta h_{\Delta P}$  (i.e.,  $\int v dP$ ) depends mostly on pressure since the specific volume,  $v$ , does not change significantly. As is evident from data in Table 3, the correction, Eq. (5) [1,2], as a general improvement for compressed liquid enthalpy calculation, is not justified in general, but for smaller temperatures only (less than 200°C). However, it is more erroneous (and thus counterproductive and misleading) for higher temperatures (above 200°C) and particularly at higher pressures, where a simple approximation (Eq. (2)), without any correction, is more accurate.

In Fig. 1, the compression of saturated liquid water, state ( $f_{\text{sat}}$ ) at 260°C, is presented for isothermal compression to state (T50) at 50 MPa, and for isentropic compression to state (s50) to the same pressure of 50 MPa (see Table 1 for property data).

Since  $du = \delta q - \delta w$  (where  $\delta w = P dv$ ), and real liquids (in this case water) are not exactly incompressible, then during isentropic compression ( $\delta q = T ds = 0$ ) there will be some negative work ( $P dv$ ) and an increase of internal energy and temperature (in this case for 11.7°C, from 260°C to 271.7°C) [3]. However, during the isothermal compression, to cool and maintain constant water temperature, there must be some heat transfer out,  $q$ , and in the process the internal energy,  $u$ , will be decreased with pressure increase at constant temperature (see the corresponding data in Tables 1 and 2; note  $\Delta h_{\Delta u} = \Delta u < 0$  if  $\Delta P > 0$ ). At high temperatures, 300°C and above, even specific enthalpy is decreasing with

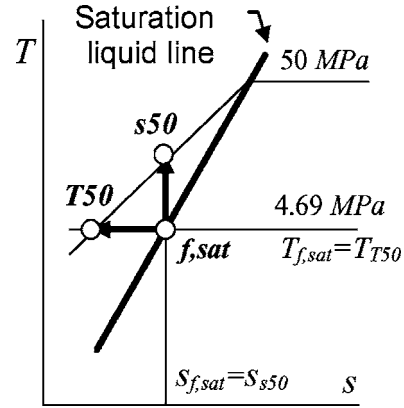


Fig. 1 Isothermal and isentropic compression of saturated liquid water

pressure increase due to a strong decrease of internal energy, making the recommended positive correction,  $\Delta h_{\text{corr}}$ , to be erroneous and thus counterproductive and misleading, see Tables 2 and 3. The  $\Delta h_{\Delta u}$  correction is not included in Eq. (5) even though its magnitude may be, and sometimes is, larger than the included  $\Delta h_{\text{corr}} \approx \Delta h_{\Delta P}$  correction. Therefore, the recommended enthalpy correction for isothermal compression in the literature is appropriate for the isentropic processes (see additional justification below), but not appropriate for isothermal processes, although it may sometimes be beneficial, due to an erroneous assumption that internal energy is not, and enthalpy is, dependent on pressure. It is quite the opposite in Table 1, see how the corresponding values ( $u$  and  $h$ ) change with pressure at constant temperature of 260°C.

The above physical justifications could be confirmed using the corresponding differential property correlations obtained using the Maxwell's relations [1]:

$$\begin{aligned} du(T, v) &= \left( \frac{\partial u}{\partial T} \right)_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv \\ &= \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv, \quad \text{for } T = \text{const} \end{aligned} \quad (9)$$

$$\begin{aligned} dh(T, P) &= \left( \frac{\partial h}{\partial T} \right)_P dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right] dP \\ &= \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right] dP, \quad \text{for } T = \text{const} \end{aligned} \quad (10)$$

From Eq. (9) it is evident that change in internal energy for the isothermal process is zero ( $du=0$ ) only for ideal incompressible fluids ( $dv=0$ ), but for real liquids ( $dv \neq 0$ ) the bracketed term with  $dv$  in Eq. (9) is not zero since real liquids are not exactly incompressible.

Equation (10) confirms that pressure correction ( $vdP$ ) is always appropriate for isentropic processes ( $dh = T ds + v dP = v dP$  for  $s = \text{const}$ ), but not for isothermal processes as given in many refer-

ences [1,2]. For example, for an isentropic compression of liquid water from saturation at 260°C to 50 MPa, see Fig. 1 and data in Table 1 ( $P_{\text{sat}}=4.69$  MPa,  $h_{\text{sat}}=1135.0$  kJ/kg,  $s_{\text{sat}}=2.8849$  kJ/kg K), the temperature and enthalpy will increase to 271.7°C and  $h_{s50}=1191.7$  kJ/kg, respectively [3]. The isentropic enthalpy increase,  $h_{s50}-h_{\text{sat}}=(1191.7-1135.0)$  kJ/kg=56.7 kJ/kg is virtually identical to the corresponding enthalpy correction ( $\Delta h_{\Delta P}=\int v dP=56.05$  KJ/kg) $\approx$  ( $\Delta h_{\text{corr}}=57.82$  kJ/kg), where the small differences in Table 1 are due to an integral approximation with discrete summation (Eq.(8)) or assuming  $v=v_{\text{sat}}=\text{const}$  in Eq. (5) during the process.

For the isothermal process the enthalpy pressure-correction could be evaluated using the three corrections, Eqs. (6)–(8), or integrating Eq. (9) or (10), or combined Eqs. (9) and (10), i.e.:

$$[\Delta h]_T = [h(P, T) - h_{\text{sat}}(T)]_T$$

$$= \begin{cases} \Delta h_{\Delta u}(\text{Eq.6}) + \Delta h_{\Delta v}(\text{Eq.7}) + \Delta h_{\Delta P}(\text{Eq.8}) \\ \int_{P_{\text{sat}}}^P \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right] dP = \int_{P_{\text{sat}}}^P \left[ -C_P \left( \frac{\partial T}{\partial P} \right)_h \right] dP \\ \int_{P_{\text{sat}}}^P v dP + \int_{v_{\text{sat}}}^v \left[ T \left( \frac{\partial P}{\partial T} \right)_v \right] dv \end{cases} \quad (11)$$

Since the Joule-Thomson coefficient is defined as  $\mu_{JT}=(\partial T/\partial P)_h$ , then Eq. (11) could be expressed as:

$$[\Delta h]_T = [h(P, T) - h_{\text{sat}}(T)]_T = \Delta h_{\Delta u} + \Delta h_{\Delta v} + \Delta h_{\Delta P}$$

$$= \int_{P_{\text{sat}}}^P [-C_P \mu_{JT}] dP$$

$$\cong \sum_{i=1}^{N-1} \left[ \frac{1}{2} (C_{P,i} \mu_{JT,i} + C_{P,i+1} \mu_{JT,i+1}) \right] (P_{i+1} - P_i) \quad (12)$$

Note that real data values for both, the  $\mu_{JT}$  and  $C_P$  are available [3], and for the isothermal enthalpy correction,  $\Delta h$ , Eq. (12) was used instead of Eqs. (6)–(8), see Table 1.

Compressed liquid water enthalpies ( $h$ ), different corrections, their approximation differences ( $h_{\text{sat}}-h$ , and  $h_{\text{corr}}-h$ ) and the corresponding error percentages, with regard to the saturation value, are presented in Table 3, without any correction (Eq. (2)) and the correction recommended in the literature ( $\Delta h_{\text{corr}} \approx \Delta h_{\Delta P}$ , Eq. (5)), for a wide range of temperatures and pressures. The corrections, as recommended in [1,2] (Eq. (5)), are only beneficial for higher pressures at smaller temperatures, insignificant for smaller pressures at most of the temperatures, about the same but opposite sign (thus unnecessary) for intermediate temperatures and pressures, and more erroneous (thus counterproductive and misleading) for higher temperatures and pressures, than the simple approximation without any correction (Eq. (2)), as seen from Tables 1 and 3.

### 3 Conclusion

An analysis with physical justification, supported by water real enthalpy data, regarding liquid enthalpy approximation, is presented here. The analysis shows, and a conclusion is drawn, that the recommendation in the classical reference textbooks for improvement of enthalpy calculation of compressed liquids, by accounting for pressure dependence, is not generally valid for isothermal processes. The misconception in the literature is a result

of the erroneous assumption that, due to incompressibility for liquids in general, the internal energy is less dependent on pressure than enthalpy. The literature recommendations may be erroneous and thus counterproductive and misleading, as is the case for liquid water at higher temperatures and pressures. For intermediate pressures and temperatures, the enthalpy corrections recommended in the literature are unnecessary, since the errors are about the same in magnitude (but opposite in sign) as if the corresponding saturated enthalpy values without any corrections were used. The isothermal corrections are only beneficial for very high pressures at smaller temperatures (below 200°C for liquid water).

In summary, the recommended pressure corrections in the classical reference textbooks for isothermal, liquid enthalpy approximation are not appropriate and often insignificant, unnecessary or more erroneous than the simple approximation using the corresponding saturated values. Furthermore, it is shown here that the recommended pressure correction for isothermal processes are actually valid in general for enthalpy correction for isentropic processes.

### Nomenclature

- $c, c_p, c_v$  = specific heat, at constant pressure, or constant volume
- $c_{\text{sound}}$  = speed of sound
- $\Delta h$  = enthalpy correction including all relevant corrections, Eq. (12)
- $\Delta h_{\text{corr}}$  = enthalpy correction due to the change of  $\Delta P_{\text{sat}} = P - P_{\text{sat}}$ , Eq. (5a)
- $\Delta h_{\Delta u}$  = enthalpy correction due to the change of  $\Delta u$ , Eq. (6)
- $\Delta h_{\Delta v}$  = enthalpy correction due to the change of  $\Delta v$ , Eq. (7)
- $\Delta h_{\Delta P}$  = enthalpy correction due to the change of  $\Delta P$ , Eq. (8)
- $h$  = liquid enthalpy at any  $P$  and  $T$
- $h_{\text{corr}}$  = liquid enthalpy approximation with  $v_{\text{sat}} \Delta P_{\text{sat}}$  correction as recommended in the literature
- $h_{\text{sat}}$  = saturation liquid enthalpy
- $P$  = pressure
- $q$  = heat transfer per unit of mass
- $s$  = entropy
- $T$  = temperature
- $u$  = internal thermal energy
- $v$  = specific volume
- $w$  = boundary work per unit of mass
- $\mu_{JT}$  = The Joule-Thomson coefficient

### Subscripts

- s50 = isentropic compression from saturated to 50 MPa
- sat = for saturated liquid
- T50 = isothermal compression from saturated to 50 MPa

### References

- [1] Cengel, Y. A., and Boles, M. A., 2002, *Thermodynamics, An Engineering Approach*, 4th ed., McGraw-Hill, New York, Sec. 2.5.3, p. 84.
- [2] Moran, M. J., and Shapiro, H. N., 2000, *Fundamentals of Engineering Thermodynamics*, 4th ed., Wiley, New York, Sec. 3.3.6, p. 109.
- [3] Lemmon, E. W., McLinden, M. O., and Friend, D. G., 2005, "Thermophysical Properties of Fluid Systems," *NIST Chemistry WebBook*, NIST Standard Reference Database No. 69, P. J. Linstrom, and W. G. Mallard, eds., National Institute of Standards and Technology, Gaithersburg, MD (<http://webbook.nist.gov/chemistry/fluid>).