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THERMODYNAMIC PROPERTIES COMPUTATION OF TWO POSSIBLE SUBSTITUTE REFRIGERANTS : R143a (1,1,1-trifluoroethane) and R125 (pentafluoroethane)

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ABSTRACT

Among new refrigerants presently under study for replacing halogenated CFC's, fluids R143a (CH_3CF_3) and R125 (CF_3CHF_2) are considered as possible alternatives for R502. To evaluate the impact of fluid replacement in existing units, it is necessary to use accurate thermodynamic data for these new refrigerants.

Through application of four basic relations, we can calculate a number of thermodynamic properties for a given fluid.

We applied these relations to CFC alternatives R143a and R125.

Equation of state was implemented under the form of Martin-Hou equation, the coefficients of which were calculated from critical properties P_c, v_c, T_c, normal boiling point temperature and molar mass.

The state equation thus obtained is in good agreement with existing experimental data for R143a .

We present thermodynamic tables for saturated vapor and liquid properties P, v, T, h, s and L_v, as well as a table for P, v, T, h, s properties for superheated vapor.

We finally give Mollier's diagrams (h-log P) for both fluids.

I. INTRODUCTION

Because of their deleterious effect on stratospheric ozone, most CFC refrigerants are to be banned in the near future. Thus the necessity of selecting new refrigerant fluids for existing units will be an often encountered problem in the next few years.

Among the fluids to be replaced is R502 (an azeotropic mixture of R22 and R115), because of the very stable chlore-fluor chemical bond in R115 molecules. Two possible substitute refrigerants are R143a and R125.

The evaluation of the consequences of such a substitution requires accurate thermodynamic models of these new fluids.

The purpose of this paper is to present the models we have derived from data available in the litterature; comparison with experimental data will be presented, and complete thermodynamic data and charts made available.

II. BASIC EQUATIONS

The adopted modelisation is based on the four following relations:

- state equation for vapor phase : $P = f(v,T)$
- saturated liquid density : $\rho_L = f(T)$

- saturated vapor pressure : $P_v = f(T)$
- specific heat in the ideal gas state : $C_v^0 = f(T)$ or $C_p^0 = f(T)$

II.1 Vapor state equation

The state equation we use has been proposed by Martin and Hou [1]:

$$P = \frac{r.T}{(v-b)} + \frac{A_2 + B_2 \cdot T + C_2 \cdot e^{-k \cdot T/T_c}}{(v-b)^2} + \frac{A_3 + B_3 \cdot T + C_3 \cdot e^{-k \cdot T/T_c}}{(v-b)^3} + \frac{A_4}{(v-b)^4} + \frac{B_5 \cdot T}{(v-b)^5}$$

The theory developed by Martin and Hou is underlied by a certain number of hypotheses concerning the behaviour of fluids. These hypotheses lead to relations (e.g. annulation of partial derivatives up to order 4 at critical point for pressure versus volume) which enable the calculation of the nine coefficients b, A_2, A_3, A_4, B_2, B_3, B_5, C_2 and C_3 from the knowledge of four physical parameters, which are the critical properties P_c, T_c, v_c, and the slope of the critical isochore at the critical point, denoted as m.

This last parameter can be obtained directly from the data for a point on the saturation curve (for instance the normal boiling temperature).

Values for these four physical parameters, as obtained from the litterature, are shown in tab.1, for refrigerants R134a and R125.

Fluid	P_c (kPa)	ρ_c (kg.m^{-3})	T_c (K)	T_{nb} (K)
R143a	3811	434	346.25	225.8
R125	3631	572	339.4	224.6

Table 1 : Fluid fixed points (from McLinden [2]).

Using these values, we calculated the coefficients for the equation of state of both fluids, by following the original procedure of Martin and Hou. The coefficients are presented in tab.2

Fluid	R125	R143a
k	5.475	5.475
b	3.585E-04	3.252E-04
r	6.927E+01	9.893E+01
A_2	-7.98629E+01	-1.63472E+02
A_3	8.99180E-02	2.72072E-01
A_4	-5.20261E-05	-2.05412E-04
B_2	7.50015E-02	1.72187E-01
B_3	-5.78122E-05	-2.43954E-04
B_5	4.03379E-11	2.17106E-10
C_2	-1.58418E+03	-4.81139E+03
C_3	2.20173E+00	9.00979E+00

Table 2 : S.I. coeficients of Martin-Hou equation of state.

<u>Remark</u> : some authors use only the form of Martin-Hou equation and correlate its coefficients with data obtained in a certain range of temperature and pression. While necessarily more accurate within this range, the equation thus obtained can lead to dubious results if extrapolated to points outside the range; conversely, the original procedure is supposed to lead to an equation valid in a large range of pressure and temperature, unless the underlying theory is found to be at fault.

We compared the results obtained through our equation with experimental data available for R134a (Mears et al.[3]; Arnaud et al.[4]). See fig. 1; to the best of our knowledge, no P-v-T data is yet available for R125.

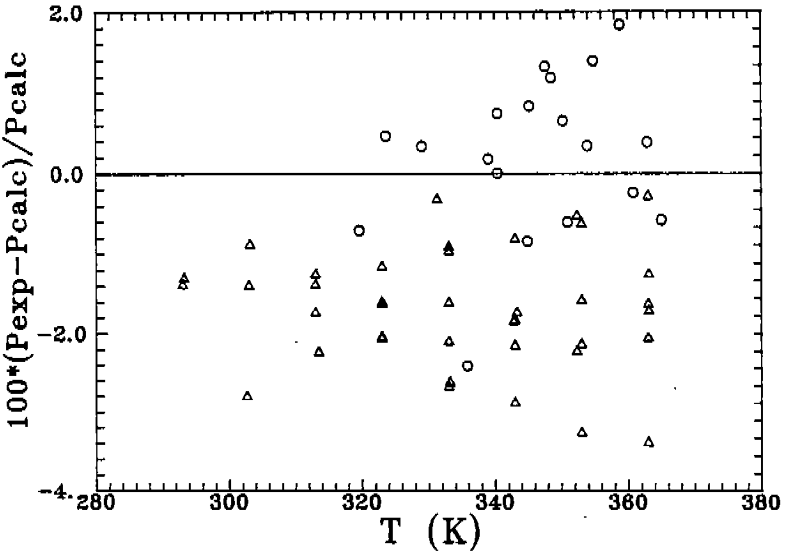

Fig. 1 : Comparison of Martin-Hou equation versus P-v-T experimental data. (o : Mears et al.[3]; Δ : Arnaud et al.[4])

Experimental P-v-T data used for this comparison are not available in numerical form, but only as charts as published by the authors; this of course limits the accuracy of the comparison.

<u>II.2. Other correlations :</u>

We used the correlations as given by McLinden [2].

II.2.1. Saturated liquid density :

$$\frac{\rho}{\rho_c} = 1 + d_1 \cdot \tau^{0.355} + d_2 \cdot \tau^{2/3} + d_3 \cdot \tau + d_4 \cdot \tau^{4/3}$$

where $\tau = (1 - T/T_c)$.

II.2.2. Vapour pressure :

$$\ln(P/P_c) = a_1 \cdot \tau/(1-\tau) + a_2 \cdot \tau + a_3 \cdot \tau^{1.89} + a_4 \cdot \tau^3$$

where $\tau=(1-T/T_c)$.

II.2.3. Ideal gas heat capacity :

$$\frac{C_p^0}{R} = c_0 + c_1 \cdot T_r + c_2 \cdot T_r^2 + c_3 \cdot T_r^3$$

where $T_r=T/T_c$ and R is the gas constant (8.3145 $J.mol^{-1}.K^{-1}$).

III. COMPUTATION OF THERMODYNAMIC PROPERTIES

All thermodynamic properties in the saturated liquid-vapor state and in the vapor phase at a given temperature and volume are easily computed from the basic equations above.

III.1. Specific heat at constant volume :

$C_v\,(v,T)$ is obtained from $C_v^0\,(T)$ by integrating at constant temperature :

$$C_v\,(v,T) = C_v^0\,(T) + T \int_{\infty}^{v} \left(\frac{\partial^2 P}{\partial T^2}\right)_v dv$$

III.2. Specific heat at constant pressure :

$C_p\,(v,T)$ is computed by application of Mayer's generalized law :

$$C_p\,(v,T) = C_v\,(v,T) - T\,\frac{\left[\left(\frac{\partial P}{\partial T}\right)_v\right]^2}{\left(\frac{\partial P}{\partial v}\right)_T}$$

III.3. Specific enthalpy :

$h\,(v,T)$ is obtained by integrating from a reference state h_{ref} first on an isovolumic path and then on an isothermal path :

$$h\,(v,T) = h_{ref} + \int_{T_{ref}}^{T} [\, C_v^0(T) + T \int_{\infty}^{v_{ref}} (\frac{\partial^2 P}{\partial T^2})_v \, dv \,]\, dT$$

$$+ \int_{v_{ref}}^{v} [\, T\,(\frac{\partial P}{\partial T})_v - p \,]_T \, dv + P\,v - P_{ref} v_{ref}$$

III.4. Specific entropy :

s (v,T) is obtained in a similar fashion to h (v,T) :

$$s\,(v,T) = s_{ref} + \int_{T_{ref}}^{T} [\, \frac{C_v^0(T)}{T} + \int_{\infty}^{v_{ref}} (\frac{\partial^2 P}{\partial T^2})_v \, dv) \,]\, dT + \int_{v_{ref}}^{v} [\, (\frac{\partial P}{\partial T})_v]_T \, dv$$

It should be noticed that all four equations above give rise to analytical expressions for C_V, C_p, h and s, provided that integral terms can be computed.

II.5. Latent heat of vaporization :

Clapeyron equation gives :

$$L_v = T \frac{dP_v(T)}{dT} (v_v - v_L),$$

This equation requires the knowledge of v(P,T) and is then the only non-explicit thermodynamic property as a function of (v,T).

IV. CONCLUSION

We give in the following pages tables for saturated and superheated properties of R125 and R134a, along with h-logP thermodynamic charts. These data were computed from the above relations and compared with such available experimental data as we could find; unfortunately these data are scarce and only presented as diagrams with no estimation of experimental errors, which prevents us from drawing conclusions about discrepancies between experimental and computed properties. Thus it appears that there is a need for more reliable experimental data concerning those fluids.

So far, the comparison between these fluids shows that their main difference lies in the values of latent heat at normal boiling point, the value for R143a being 30% larger than that for R125.

NOMENCLATURE			
h	: specific enthalpy	C_v	: specific heat at constant volume
M	: molar mass	C_p	: specific heat at constant pressure
P	: absolute pressure	L_v	: latent heat of vaporization
R	: perfect gas constant	*Greek letters :*	
r	= R/M	ρ	: density
s	: specific entropy	*Subscripts :*	
T	: temperature	c	: thermodynamic critical point
v	: specific volume	v	: saturated vapor
Superscripts :		L	: saturated liquid
^{o}	: ideal gas state	nb	: normal boiling point

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R143a Tc : 72.85°C Pc : 3787 kPa

		Vapor				Liquid		
T °C	P kPa	v_v g/m^3	h_v kJ/kg	s_v kJ/kg.K	L_v kJ/kg	v_L kg/m^3	h_L kJ/kg	s_L kJ/kg.K
-80	16.05	1171.589	338.68	1.813	244.91	0.823	93.77	0.545
-75	22.28	862.627	341.81	1.797	242.15	0.828	99.66	0.575
-70	30.36	646.017	344.94	1.783	239.28	0.834	105.66	0.605
-65	40.67	491.376	348.05	1.770	236.28	0.840	111.77	0.635
-60	53.65	379.112	351.15	1.758	233.15	0.847	118.00	0.664
-55	69.75	296.340	354.23	1.747	229.90	0.854	124.33	0.693
-50	89.49	234.431	357.28	1.738	226.51	0.861	130.76	0.723
-45	113.39	187.504	360.29	1.729	223.00	0.870	137.29	0.751
-40	142.05	151.490	363.26	1.721	219.34	0.878	143.92	0.780
-35	176.07	123.529	366.19	1.714	215.55	0.888	150.63	0.808
-30	216.07	101.585	369.06	1.707	211.63	0.898	157.43	0.836
-25	262.73	84.188	371.88	1.701	207.56	0.908	164.32	0.864
-20	316.74	70.265	374.63	1.695	203.35	0.920	171.28	0.892
-15	378.81	59.023	377.32	1.690	198.98	0.933	178.33	0.919
-10	449.68	49.868	379.93	1.685	194.46	0.946	185.47	0.946
-5	530.12	42.353	382.45	1.681	189.76	0.960	192.69	0.973
0	620.92	36.139	384.88	1.677	184.88	0.976	200.00	1.000
5	722.89	30.962	387.21	1.673	179.80	0.993	207.41	1.027
10	836.89	26.621	389.41	1.669	174.48	1.011	214.93	1.053
15	963.82	22.954	391.47	1.665	168.91	1.032	222.56	1.079
20	1104.60	19.838	393.38	1.662	163.04	1.054	230.34	1.105
25	1260.24	17.173	395.09	1.658	156.83	1.078	238.26	1.132
30	1431.78	14.878	396.57	1.653	150.20	1.105	246.37	1.158
35	1620.38	12.889	397.78	1.649	143.09	1.135	254.69	1.185
40	1827.29	11.152	398.64	1.644	135.37	1.169	263.26	1.211
45	2053.90	9.623	399.05	1.638	126.90	1.207	272.15	1.239
50	2301.84	8.264	398.88	1.630	117.46	1.252	281.42	1.267
55	2572.99	7.040	397.90	1.621	106.69	1.306	291.21	1.296
60	2869.78	5.914	395.69	1.608	94.00	1.372	301.69	1.326
65	3195.57	4.840	391.40	1.590	78.13	1.462	313.27	1.359
70	3556.58	3.701	382.15	1.559	54.87	1.613	327.27	1.399

R125 Tc : 66.25 °C Pc : 3631 kPa

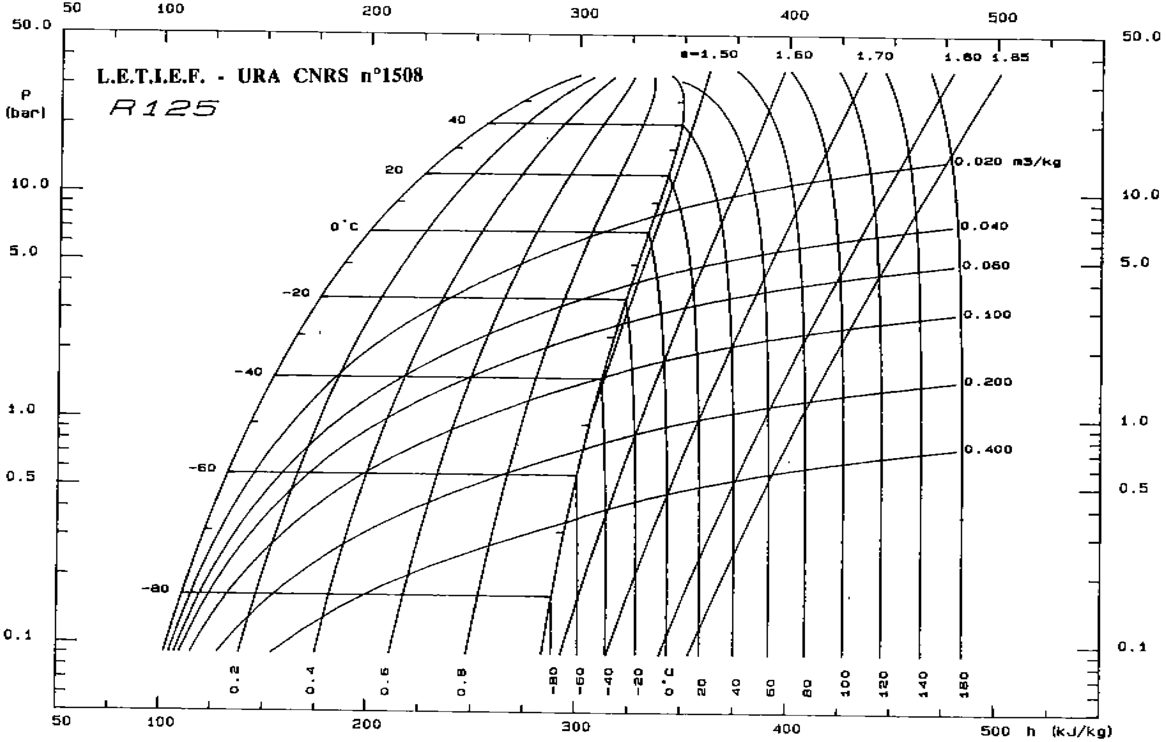
		Vapor				Liquid		
T °C	P kPa	v_v g/m^3	h_v kJ/kg	s_v kJ/kg.K	L_v kJ/kg	v_L kg/m^3	h_L kJ/kg	s_L kJ/kg.K
-80	16.28	811.754	288.36	1.535	177.36	0.617	111.00	0.6174
-75	22.81	592.515	291.25	1.527	174.84	0.623	116.41	0.6450
-70	31.32	440.635	294.15	1.520	172.33	0.630	121.82	0.6720
-65	42.24	333.283	297.06	1.514	169.83	0.636	127.23	0.6982
-60	56.01	255.992	299.96	1.508	167.32	0.643	132.64	0.7239
-55	73.15	199.390	302.87	1.504	164.81	0.650	138.06	0.7490
-50	94.21	157.288	305.76	1.500	162.27	0.658	143.49	0.7735
-45	119.78	125.515	308.64	1.497	159.70	0.666	148.94	0.7976
-40	150.50	101.216	311.51	1.495	157.10	0.674	154.41	0.8212
-35	187.04	82.401	314.35	1.493	154.45	0.682	159.90	0.8444
-30	230.11	67.665	317.17	1.491	151.74	0.691	165.43	0.8673
-25	280.47	55.999	319.96	1.490	148.95	0.701	171.01	0.8898
-20	338.92	46.673	322.71	1.489	146.07	0.711	176.64	0.9122
-15	406.30	39.146	325.42	1.488	143.08	0.721	182.34	0.9343
-10	483.46	33.019	328.08	1.488	139.96	0.733	188.13	0.9562
-5	571.34	27.991	330.69	1.487	136.68	0.745	194.01	0.9781
0	670.87	23.832	333.22	1.487	133.22	0.757	200.00	1.0000
5	783.05	20.367	335.68	1.487	129.55	0.771	206.13	1.0219
10	908.90	17.460	338.04	1.487	125.63	0.786	212.42	1.0440
15	1049.50	15.004	340.29	1.487	121.41	0.802	218.88	1.0662
20	1205.97	12.915	342.41	1.487	116.85	0.820	225.56	1.0888
25	1379.45	11.127	344.36	1.486	111.88	0.840	232.48	1.1117
30	1571.14	9.586	346.12	1.486	106.42	0.862	239.69	1.1351
35	1782.30	8.247	347.62	1.484	100.37	0.888	247.24	1.1592
40	2014.21	7.074	348.79	1.483	93.60	0.918	255.19	1.1841
45	2268.24	6.036	349.52	1.480	85.88	0.953	263.64	1.2102
50	2545.83	5.102	349.63	1.475	76.88	0.998	272.75	1.2377
55	2848.51	4.242	348.76	1.468	65.99	1.058	282.77	1.2675
60	3178.01	3.407	346.05	1.456	51.70	1.149	294.35	1.3014
65	3536.48	2.423	337.39	1.427	26.87	1.360	310.51	1.3482

P (kPa)	T (°C)	+0°C	+10°C	+20°C	+30°C	+40°C	+50°C	+60°C	+70°C	+80°C	+90°C	+100°C	
40	-65.93	296.5 1.515 0.351	303.1 1.547 0.369	309.9 1.577 0.387	316.9 1.607 0.405	324.0 1.636 0.423	331.3 1.665 0.441	338.7 1.694 0.459	346.3 1.722 0.476	354.1 1.749 0.494	362.0 1.776 0.512	370.1 1.803 0.529	h(kJ/kg) s(kJ/kg.K) $v(m^3/kg)$
80	-53.26	303.8 1.503 0.183	310.8 1.534 0.193	317.9 1.564 0.202	325.2 1.594 0.211	332.6 1.623 0.221	340.2 1.652 0.230	347.9 1.680 0.239	355.7 1.707 0.248	363.7 1.734 0.257	371.9 1.761 0.266	380.2 1.788 0.274	
160	-38.62	312.3 1.494 0.096	319.7 1.525 0.101	327.2 1.556 0.105	334.8 1.585 0.110	342.6 1.614 0.115	350.5 1.642 0.120	358.5 1.670 0.124	366.7 1.697 0.129	375.0 1.724 0.133	383.4 1.750 0.138	392.0 1.776 0.142	
240	-28.96	317.8 1.491 0.065	325.5 1.522 0.069	333.3 1.552 0.072	341.2 1.582 0.075	349.2 1.610 0.078	357.4 1.638 0.082	365.6 1.666 0.085	374.0 1.693 0.088	382.5 1.720 0.091	391.1 1.746 0.094	399.9 1.772 0.097	
320	-21.54	321.8 1.489 0.049	329.8 1.521 0.052	337.9 1.551 0.055	346.0 1.580 0.057	354.2 1.609 0.060	362.5 1.637 0.062	371.0 1.664 0.065	379.5 1.691 0.067	388.2 1.718 0.069	396.9 1.744 0.072	405.8 1.770 0.074	
480	-10.21	328.0 1.488 0.033	336.4 1.520 0.035	344.9 1.550 0.037	353.4 1.580 0.039	361.9 1.608 0.041	370.5 1.636 0.042	379.2 1.664 0.044	388.0 1.690 0.046	396.9 1.717 0.047	405.9 1.743 0.049	415.1 1.768 0.050	
640	-1.49	332.4 1.488 0.025	341.3 1.520 0.027	350.1 1.550 0.028	358.8 1.580 0.029	367.6 1.609 0.031	376.5 1.637 0.032	385.4 1.664 0.033	394.4 1.691 0.035	403.5 1.717 0.036	412.7 1.743 0.037	422.1 1.768 0.038	
960	11.88	338.9 1.488 0.016	348.5 1.521 0.018	357.8 1.552 0.019	367.1 1.582 0.020	376.4 1.611 0.021	385.6 1.639 0.022	394.9 1.666 0.023	404.3 1.693 0.023	413.7 1.719 0.024	423.2 1.745 0.025	432.8 1.770 0.026	
1280	22.20	343.2 1.487 0.012	353.5 1.521 0.013	363.4 1.553 0.014	373.2 1.584 0.015	382.8 1.613 0.016	392.4 1.641 0.016	402.0 1.669 0.017	411.6 1.695 0.018	421.3 1.721 0.018	431.1 1.747 0.019	440.9 1.772 0.020	
1920	38.02	348.4 1.484 0.008	360.3 1.521 0.008	371.3 1.555 0.009	381.9 1.587 0.010	392.2 1.617 0.010	402.4 1.645 0.011	412.6 1.673 0.011	422.7 1.700 0.012	432.8 1.726 0.012	443.0 1.752 0.013	453.2 1.777 0.013	
2560	50.24	349.6 1.475 0.005	364.0 1.519 0.006	376.4 1.556 0.007	387.8 1.589 0.007	398.9 1.620 0.008	409.6 1.649 0.008	420.3 1.677 0.009	430.8 1.704 0.009	441.3 1.730 0.009	451.8 1.756 0.010	462.3 1.781 0.010	

R125

P (kPa)	T (°C)	+0°C	+10°C	+20°C	+30°C	+40°C	+50°C	+60°C	+70°C	+80°C	+90°C	+100°C	
40	-65.29	347.8 1.771 0.499	355.6 1.807 0.526	363.6 1.843 0.552	371.7 1.878 0.579	380.1 1.912 0.604	388.6 1.946 0.630	397.4 1.979 0.656	406.4 2.012 0.681	415.5 2.045 0.706	424.9 2.077 0.732	434.4 2.108 0.757	h(kJ/kg) s(kJ/kg K) $v(m^3/kg)$
80	-52.28	355.8 1.742 0.261	364.2 1.779 0.275	372.6 1.815 0.288	381.3 1.850 0.302	390.1 1.884 0.315	399.0 1.918 0.328	408.2 1.951 0.341	417.5 1.984 0.354	427.0 2.016 0.367	436.7 2.047 0.380	446.6 2.079 0.393	
160	-37.26	364.8 1.717 0.135	373.9 1.754 0.143	383.0 1.791 0.150	392.2 1.826 0.157	401.6 1.860 0.164	411.0 1.894 0.171	420.6 1.927 0.178	430.4 1.960 0.184	440.3 1.992 0.191	450.4 2.023 0.198	460.7 2.054 0.204	
240	-27.34	370.6 1.704 0.092	380.2 1.742 0.097	389.8 1.779 0.102	399.4 1.814 0.107	409.1 1.849 0.112	419.0 1.883 0.117	428.9 1.916 0.121	439.0 1.948 0.126	449.2 1.980 0.130	459.5 2.011 0.135	470.1 2.042 0.139	
320	-19.72	374.7 1.695 0.070	384.8 1.734 0.074	394.8 1.771 0.078	404.8 1.807 0.082	414.8 1.842 0.085	424.9 1.876 0.089	435.2 1.909 0.092	445.5 1.941 0.096	455.9 1.973 0.099	466.5 2.004 0.103	477.2 2.035 0.106	
480	-8.04	380.9 1.684 0.047	391.8 1.724 0.050	402.4 1.762 0.053	413.0 1.798 0.055	423.6 1.833 0.058	434.1 1.868 0.060	444.8 1.901 0.063	455.5 1.933 0.065	466.3 1.965 0.068	477.2 1.996 0.070	468.2 2.027 0.072	
640	0.98	385.3 1.676 0.035	396.8 1.717 0.038	408.1 1.756 0.040	419.1 1.793 0.042	430.1 1.829 0.044	441.1 1.863 0.046	452.0 1.896 0.048	463.0 1.929 0.050	474.1 1.961 0.052	485.3 1.992 0.053	496.6 2.022 0.055	
960	14.86	391.4 1.665 0.023	404.2 1.709 0.025	416.5 1.750 0.027	428.3 1.788 0.028	440.0 1.824 0.030	451.6 1.858 0.031	463.1 1.892 0.032	474.6 1.925 0.034	486.2 1.957 0.035	497.8 1.988 0.036	509.5 2.018 0.037	
1280	25.60	395.2 1.657 0.017	409.3 1.704 0.018	422.4 1.745 0.020	435.0 1.784 0.021	447.3 1.821 0.022	459.4 1.856 0.023	471.4 1.890 0.025	483.4 1.923 0.026	495.3 1.955 0.027	507.3 1.986 0.028	519.3 2.017 0.028	
1920	42.10	398.9 1.641 0.010	415.8 1.694 0.012	430.8 1.739 0.013	444.7 1.780 0.014	458.1 1.819 0.015	471.1 1.855 0.016	483.8 1.889 0.016	496.5 1.922 0.017	509.0 1.955 0.018	521.5 1.986 0.019	534.1 2.016 0.019	
2560	54.77	397.9 1.621 0.007	419.1 1.685 0.008	436.0 1.734 0.009	451.2 1.777 0.010	465.5 1.817 0.011	479.3 1.854 0.012	492.8 1.889 0.012	506.0 1.923 0.013	519.1 1.955 0.013	532.1 1.986 0.014	545.9 2.017 0.015	

R143a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R125
P (bar)
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10.0
5.0
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0.5
0.1
50
100
200
300
400
500
h (kJ/kg)
s=1.50
1.60
1.70
1.80
1.85
40
20
0°C
-20
-40
-60
-80
0.020 m3/kg
0.040
0.060
0.100
0.200
0.400
0.2
0.4
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0°C
20
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60
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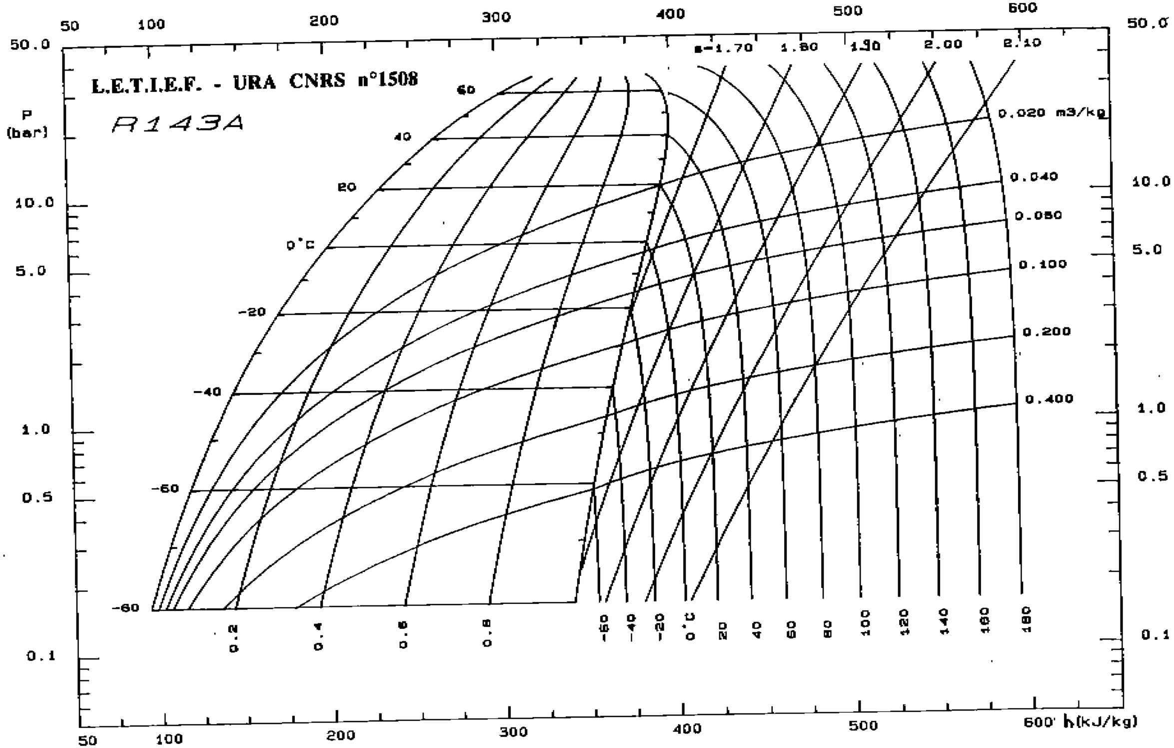
100
120
140
180


L.E.T.I.E.F. - URA CNRS n°1508
R143A
P (bar)
h (kJ/kg)
50
100
200
300
400
500
600
50.0
10.0
5.0
1.0
0.5
0.1
s=1.70
1.80
1.90
2.00
2.10
0.020 m3/kg
0.040
0.060
0.100
0.200
0.400
60
40
20
0°C
-20
-40
-60
-60
0.2
0.4
0.6
0.8
-60
-40
-20
0°C
20
40
60
80
100
120
140
160
180