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Development of Properties Database of Carbon Dioxide Refrigerant

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Abstract

At the beginning of the 20th century, refrigeration was well-established on an industrial scale but researchers still finding the best refrigerant to be used in widely application. This is because due to the people start to invent a system such as air conditioning and refrigeration using suitable refrigerant. People may famous with refrigerant R-134a that has been used all over the world in refrigeration and air conditioning system. But still, they have their own disadvantages that unsuitable to mankind. Now, for Carbon Dioxide (R744) refrigerant will become a trend in industries. A few advantages of Carbon Dioxide help people to choose as a refrigerant. Hence, a published table for Carbon Dioxide (R744) refrigerant had to be created. This table is properties databases that contain all properties and states of Carbon Dioxide. The following set of tables contain all properties will be develop by using Visual Basic version 6 software. A suitable format will be organized to make sure this database is a friendly application and can be used by all kind of researchers in industries.

***Keyword**: refrigerant, carbon dioxide, properties.*

1. Introduction

The working fluids used in applications such as refrigeration cycles are called refrigerant. Haaf and Henrici (2002) stated that a refrigerant is a substance used in a heat cycle usually including, for enhanced efficiency, a reversible phase change from a gas to a liquid. The ideal refrigerant has good thermodynamic properties, is not reactive chemically and safe. The desired thermodynamic properties are a boiling point somewhat below the target temperature, a high heat of vaporization, a moderate density in liquid form, a relatively high density in gaseous form and a high critical temperature. Since boiling point and gas density are affected by pressure, refrigerants may be made more suitable for a particular application by choice of operating pressure.

The new refrigerants must not contain chlorine, because it was chlorine which was damaging the ozone layer. The new refrigerants must also be efficient in use because attention was turning to the consequences of power requirement on global warming. Finally, and ideally, the new refrigerants themselves should have low direct global warming impacts on their release (Pearson, 2004; Calm, 2008; Pavkovic, 2013).

The beginning of the refrigerant is in the middle of 20^{th} century during the industrial revolution when people began to understand the basic facts of thermodynamics. The use of refrigerant becomes common use in widely application when the people are tend to invent system such as air-conditioning, heat pump and refrigerators. In these system cycles, the refrigerant acts as working fluid. Most common refrigerant are composed of or a combination of CFC, HFC, HCFC, CO_2 and Hydrocarbon.

The most famous refrigerant that still used in widely application is R-134a, which is the combination of hydrogen, fluorine and carbon (HFC). But, due to the environmental view and some drawbacks of HFC, this refrigerant may have dangerous behavior to be inconsiderable for mankind used. So, this situation has led to increase use of the “old” refrigerants ammonia and hydrocarbons. In industries, people are getting used of R-143a table that have been develop by many organizations and certain people. Now, for Carbon Dioxide (R744) refrigerant will become more universal to industries. Hence, creating the published tables for Carbon Dioxide (R744) refrigerant for mankind used are required. The following set of tables contain all properties will be develop by using Visual Basic version 6 software. It will be organized in a suitable format and coding for evaluating refrigeration, heat pump and air-conditioning system.

2. Carbon Dioxide

The use of carbon dioxide as a refrigerant has seen increasing interest in recent years. Carbon dioxide (CO_2) has been proposed by the Prof. Gustav Lorentzen in 1990 to be used as an alternative refrigerant, mainly because of its non flammability. This is because due to the environmental concern regarding chlorofluoro-carbons (CFCs) have depleted the earth’s ozone layer and their behavior as greenhouse gases in the atmosphere.

As shown in Figure 1 and Table 1, contrary to CFCs and HCFCs, ammonia, hydrocarbons and CO_2 all have an ozone depletion potential (ODP) of zero and a negligible global warming potential (GWP). As for HFCs, their ODP is zero and their GWP ranges from a few hundred in the case of the flammable HFC32 to several thousand in the case of the flammable HFC143a and the non-flammable R125. With respect to the local safety of "old" refrigerants**,** only CO_2 can compete with the non-flammable HFCs**.** However, contrary to HFCs, its GWP is negligible when applied as a refrigerant. Therefore, being environmentally benign and locally safe, CO_2 as a refrigerant has major benefits.

The main drawback of carbon dioxide as a refrigerant is its inherent high working pressure: this pressure is much higher than that of the other natural and synthetic refrigerants mentioned. On one hand, this means that for CO_2 cycles, newly developed components must be redesigned. Since CO_2 offers a much higher volumetric capacity, the problem of the higher working pressure can be overcome by optimal design involving smaller, stronger components.

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The CO_2 technology can meet the environmental and safety requirements of today's challenges for refrigeration, air-conditioning and heat-pump systems, but only in suitable applications where the advantages outweigh the drawbacks of this technology.

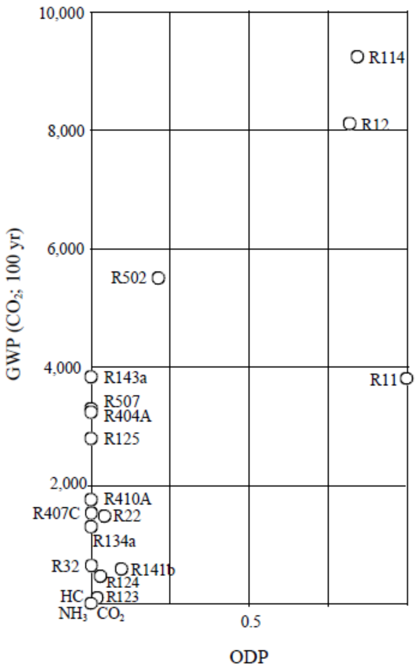


Figure 1. ODP and GWP of several refrigerants

Table 1. Comparison of CO_2 properties with those of other refrigerants

Refrigerant	R12	R22	R134a	R290	NH_3	CO_2
Natural fluid	No	No	No	Yes	Yes	Yes
ODP[3]	0.82	0.055	0	0	0	0
GWP (100yr) IPCC values[3] GWP (100yr) WMO values[4]	8100 10600	1500 1900	1300 1600	20 20	<1 <1	1 1
Critical temp. (°C)[3]	112.0	96.2	101.2	96.7	132.3	31.1
Critical pressure (MPa)[3]	4.14	4.99	4.06	4.25	11.27	7.38
Flammable	No	No	No	Yes	Yes	No
Toxic	No	No	No	No	Yes	No
Relative price	-	1.0	4.0	0.3	0.2	0.1
Volumetric capacity	1.0	1.6	1.0	1.4	1.6	8.4

Selection of any refrigerant is a compromise. Because there are many applications of refrigeration, a bewildering variety of refrigerant blends has arisen to meet these applications. Current requirements for a successful blend are that it should have an ozone depleting potential (ODP) of zero, that it should be efficient to use in conventional refrigeration machinery, that is should be non-toxic, non-flammable, and that it should have low global warming potential (GWP). It is very difficult to meet all these requirements. A major disadvantage of all the HFC refrigerants is that they have relatively high GWPs compared to the natural refrigerants.

3. Thermodynamic Properties

Carbon dioxide (CO_2) is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. CO_2 is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm. In nature, CO_2 is used by plants during photosynthesis to make sugars, which may either be consumed in respiration or used as the raw material to produce other organic compounds needed for plant growth and development.

The physical properties of carbon dioxide are a colourless and odourless gas, soluble in water, in ethanol and in acetone. CO_2 has the melting point -55.6℃ and boiling point is -78.5℃. Carbon dioxide has no liquid state at pressures below 5.1 atmospheres. At 1 atmosphere (near mean sea level pressure), the gas deposits directly to a solid at temperatures below −78°C (−108.4°F; 195.1 K) and the solid sublimes directly to a gas above −78°C. In its solid state, carbon dioxide is commonly called dry ice.

Before developing the database of $CO_{2,}$ the most important thing knows the thermodynamic properties of carbon dioxide. From this, the phase diagram will be determined and all the phases position will be construct on the database. The Table 2 shows the properties of carbon dioxide.

Table 2. Properties of Carbon Dioxide

Metric Units			Boiling Point @ 101.325 kPa		Gas Phase Properties @ 0° C & @ 101.325 kPa			Liquid Phase Properties @ B.P., & @ 101.325 kPa		Triple Point		Critical Point		
			Temp.	Latent Heat of Vaporization	Specific Gravity	Specific Heat (Cp)	Density	Specific Gravity	Specific Heat (Cp)	Temp.	Pressure	Temp.	Pressure	Density
Substance	Chemical Symbol	Mol. Weight	°C	kJ/kg	Air = 1	kJ/kg ° C	kg/m3	Water = 1	kJ/kg ° C	°C	kPa abs	° C	kPa abs	kg/m3
Carbon Dioxide	CO_2	44.01	-78.5	571.3	1.539	0.85	1.9769	1.18^{c}	--	-56.6	517.3	31.1	7382	468

The phase diagram of CO_2 has some common features with that of water: sublimation curve, vaporization curve, triple point, critical temperature and pressure. Of course, the *P* and *T* values of are unique to carbon dioxide. The phase diagrams of water and carbon dioxide are compared here. The triple point of carbon dioxide occurs at a pressure of 5.2 atm and -56.4^{o}C. At temperature of -78.5^{o}C, the vapor pressure of solid carbon dioxide is 1 atm. At this pressure, the liquid phase is not stable, the solid simply sublimates. Thus solid carbon dioxide is called dry ice, because it does not go through a liquid state in its phase transition at room pressure. The critical temperature for carbon dioxide is 31.1°C, and the critical pressure is 73 atm. Above the critical temperature, the fluid is called super-critical fluid. The Figure 2 reveals the phase diagram of carbon dioxide.

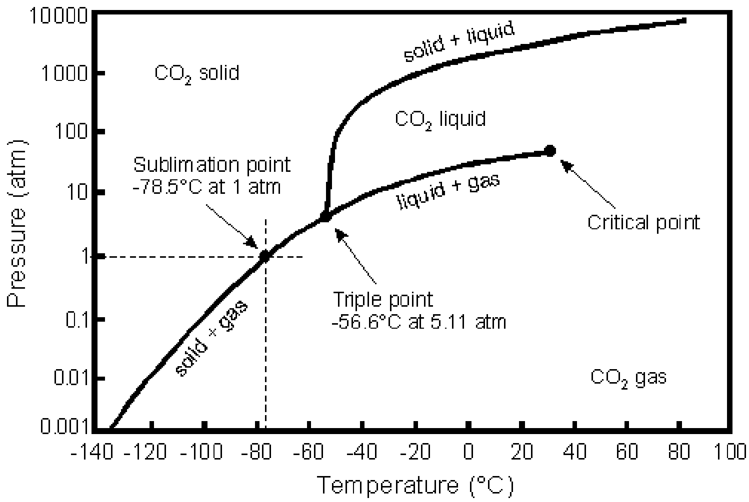


Figure 2. Pressure-temperature phase diagram for CO_2

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Therefore, properties are frequently presented in the form of tables. Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties. The results of these measurements and calculations are presented in tables in a convenient format.

For each substance, the thermodynamic properties are listed in more than one table. In fact, a separate table is prepared for each region of interest such as the superheated vapor, compressed liquid, and saturated (mixture) regions. Property tables are given in the appendix in both SI and English units.

3.1. Enthalpy and Entropy

The table of the refrigerant will notice two major properties: enthalpy (h) and entropy (s). In the analysis of certain types of processes the encounter the combination of properties that are frequently used is U + PV. This combination is defined as a new property, enthalpy, and given the symbol of H:

$$H = U + PV \text{ (kJ)} \quad (1)$$

Or, per unit mass,

$$h = u + Pv \text{ (kJ/kg)} \quad (2)$$

The entropy for pure substance change and isentropic relations for a process can be summarized as follows:

Any process: $\Delta s = s_2 - s_1$ (kJ/kg · K) (3)

Isentropic process: $s_2 = s_1$

3.2. Saturated Liquid and Saturated Vapor States

The properties of saturated liquid and saturated vapor for water are listed in two different tables. The used of both tables will be decided through the input that will be inserting. This table must be containing the specific volume of each state. For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f (that is, $v_{fg} = vg + v_f$)

3.3. Saturated Liquid–Vapor Mixture

During a vaporization process, a substance exists as part liquid and part vapor. To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture (Figure 3 and 4). This is done by defining a new property called the quality x as the ratio of the mass of vapor to the total mass of the mixture:

$$x = m_{vapor} \div m_{total} \tag{4}$$

where

$$m_{total} = m_{liquid} + m_{vapor} = m_f + m_g \tag{5}$$

Consider that a contain a saturated liquid–vapor mixture. The volume occupied by saturated liquid is v_f, and the volume occupied by saturated vapor is v_g. The total volume v is the sum of the two:

$$v = v_f + v_g \tag{6}$$

$$v = mv \longrightarrow m_t v_{avg} = m_f v_f + m_g v_{avg} \tag{7}$$

$$m_f = m_t - m_g \longrightarrow m_t v_{avg} = (m_t - m_g) v_f + m_g v_g \tag{8}$$

Dividing by m_t yields

$$v_{avg} = (1 - x) v_f + x_{vg} \tag{9}$$

Since $x = m_g / m_t$. This relation can also be expressed as

$$v_{avg} = v_f + x v_{fg} \quad (m^3/kg) \tag{10}$$

Where $v_{fg} = v_g + v_f$. Solving for quality, we obtain

$$x = (v_{avg} - v_f)/v_{fg} \tag{11}$$

The analysis given above can be repeated for internal energy and enthalpy with the following results:

$$u_{avg} = u_f + x u_{fg} \text{ (kJ/kg)} \tag{12}$$

$$h_{avg} = h_f + x h_{fg} \text{ (kJ/kg)} \tag{13}$$

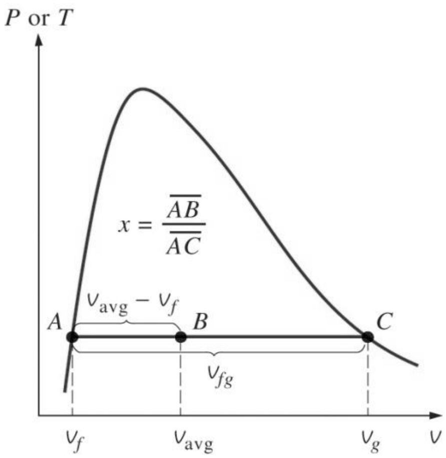


Figure 3. Quality is related to the horizontal distances on *P*-*v* and *T*-*v* diagrams

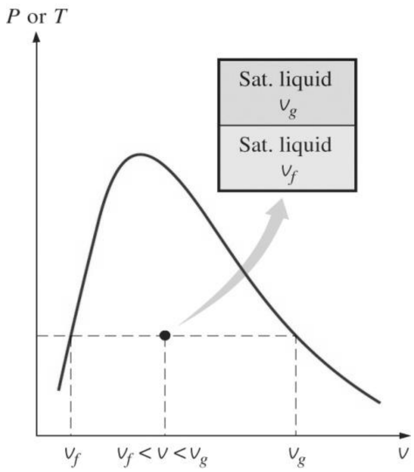


Figure 4. The v value of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified T or P

3.4. Superheated Vapor

In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor. Since the superheated region is a single-phase region (vapor phase only), temperature and pressure are no longer dependent properties and they can conveniently be used as the two independent properties in the tables. The format of the superheated vapor tables is illustrated in Table 3.

In Tables 3, the properties are listed against temperature for selected pressures starting with the saturated vapor data. The saturation temperature is given in parentheses following the pressure value. Superheated vapor is characterized by:

Lower pressures ($P<P_{sat}$ at a given T)

Higher temperatures ($T>T_{sat}$ at a given P)

Higher specific volumes ($v > v_g$ at a given P or T)

Higher internal energies ($u > u_g$ at a given P or T)

Higher enthalpies ($h > h_g$ at a given P or T)

Table 2. Format of a superheated vapor table

T,°C	v m³/kg	u kJ/kg	h kJ/kg
	P = 0.1 MPa (99.61°C)		
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
⋮	⋮	⋮	⋮
1300	7.2605	4687.2	5413.3
	P = 0.5 MPa (151.83°C)		
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

4. Program Planning

The simple program planning that will construct a database program and the step-by-step process from input until desired output. The following step-by-step process will enable programmer to design error free program.

a. Analyze: Define the problem.

The major problem that will be face in this program is determined the precise inputs and outputs. If the input are wrong, the entire database cannot be establish. The input and output in this program are temperature and pressure. A complete table can be creating through this parameter.

b. Design: Plan the solution of the problem.

First, we have to create the logical sequence of precise steps that can solve the problem. The sequence of steps is called algorithm. Every detail, including obvious steps should appear in the algorithm.

c. Choose the interface: Select the object (text box, command buttons, etc.).

It determines how the input will be obtained and how the output will be displayed. Then creates the object to receive the input and displayed the output.

d. Coding: Translate the algorithm into a programming language.

The most important part. Coding is the technical word for writing the program. During this stage, the program is written in Visual Basic and entered to the computer.

e. Test and debug: Locate and remove any errors in the program.

Testing is the process of finding the errors in program, and debugging is the process of correcting errors that are found. An error is called a bug. From the calculation and interpolation, all the data must be correct to ensure the tables that will be develop is containing error free.

f. Complete the documentation: Organize all the material that describes the program.

This last step is process to allow another person or programmer in later date understands the database of the $CO_{2.}$ The documentation might be consists of a detailed description of what the program does and how to use the program. Mostly, the person that involved in thermodynamic industries can apply their knowledge easily and use the database confidently.

5. The Properties Database

In these early days, carbon dioxide will be common in world wide as a refrigerant in industries application. So, we need published tables for Carbon Dioxide (R744) refrigerant. The tables must be well develop and contain all the properties of Carbon Dioxide including the state in different pressure and temperature. The database of the properties have to be develop by a suitable software that can reveal the all the properties of the refrigerant. The most advance software that suit with the programming is Visual Basic version 6 (VB6).

VB6 is the third-generation event-driven programming language and integrated development environment (IDE) from Microsoft for its COM programming model. VB6 is also considered a relatively easy to learn and use programming language, because of its graphical development features and BASIC heritage. Belena (2002) stated that VB6 evolved from BASIC (Beginners' All-Purpose Symbolic Instruction Code), develop in the middle 1960s by Professor John Kemeny as a language for writing simple program quickly and easily.

We need to design the front page of the program before create any form of properties. Each interface of VB6 program usually will be named form. The model contains 3 forms that represent the properties of objects. Figure 5, 6 and 7 will represents the forms.

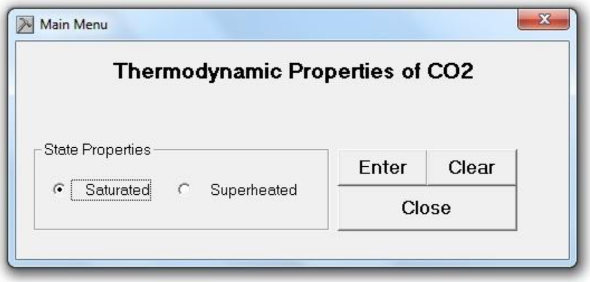


Figure 5. Front page of program

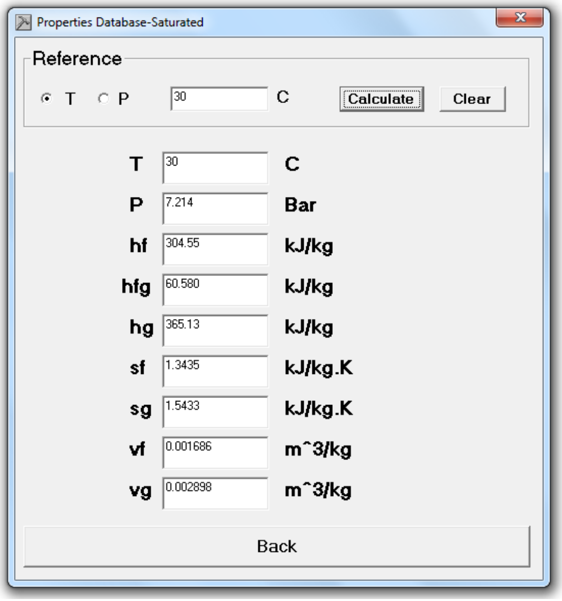


Figure 6. Saturated properties

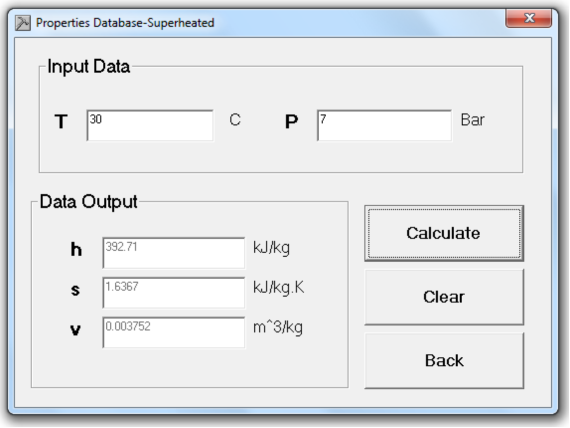


Figure 7. Superheated Properties

All properties of thermodynamic data must be arranged properly. At least in Excel version. It will easily help to transform all those data into data base in Microsoft Access.

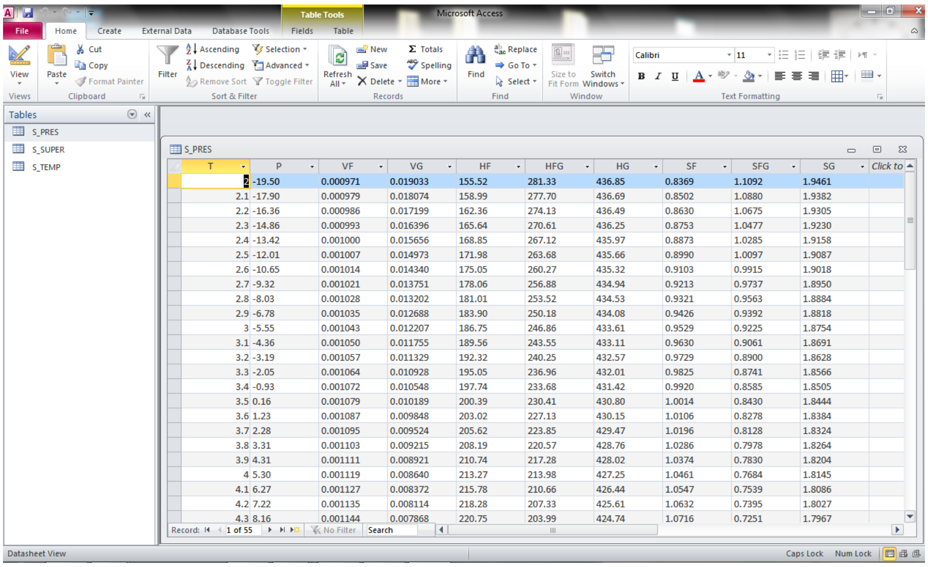
CO_2 Property Tables (Excel Version):

- Saturation Properties (Temperature Table)
- Saturation Properties (Pressure Table)
- Superheated Properties

CO_2 properties of tables:

- Saturation Properties - Temperature Table (-20°C - 30.978°C)
- Saturation Properties - Pressure Table (2 MPa - 7.377 MPa)
- Superheated Vapor Properties - (2.0 MPa - 7.0 MPa)
- Transcritical Vapor Properties - (8.0 MPa - 20.0 MPa)

After database of all properties have been created, copy the saved file then paste into local disk c. The database will be called out after fully program is established. Figure 8 is the sample of database in Microsoft Access.



S_PRES

T	P	VF	VG	HF	HFG	HG	SF	SFG	SG
2	-19.50	0.000971	0.019033	155.52	281.33	436.85	0.8369	1.1092	1.9461
2.1	-17.90	0.000979	0.018074	158.99	277.70	436.69	0.8502	1.0880	1.9382
2.2	-16.36	0.000986	0.017199	162.36	274.13	436.49	0.8630	1.0675	1.9305
2.3	-14.86	0.000993	0.016396	165.64	270.61	436.25	0.8753	1.0477	1.9230
2.4	-13.42	0.001000	0.015656	168.85	267.12	435.97	0.8873	1.0285	1.9158
2.5	-12.01	0.001007	0.014973	171.98	263.68	435.66	0.8990	1.0097	1.9087
2.6	-10.65	0.001014	0.014340	175.05	260.27	435.32	0.9103	0.9915	1.9018
2.7	-9.32	0.001021	0.013751	178.06	256.88	434.94	0.9213	0.9737	1.8950
2.8	-8.03	0.001028	0.013202	181.01	253.52	434.53	0.9321	0.9563	1.8884
2.9	-6.78	0.001035	0.012688	183.90	250.18	434.08	0.9426	0.9392	1.8818
3	-5.55	0.001043	0.012207	186.75	246.86	433.61	0.9529	0.9225	1.8754
3.1	-4.36	0.001050	0.011755	189.56	243.55	433.11	0.9630	0.9061	1.8691
3.2	-3.19	0.001057	0.011329	192.32	240.25	432.57	0.9729	0.8900	1.8628
3.3	-2.05	0.001064	0.010928	195.05	236.96	432.01	0.9825	0.8741	1.8566
3.4	-0.93	0.001072	0.010548	197.74	233.68	431.42	0.9920	0.8585	1.8505
3.5	0.16	0.001079	0.010189	200.39	230.41	430.80	1.0014	0.8430	1.8444
3.6	1.23	0.001087	0.009848	203.02	227.13	430.15	1.0106	0.8278	1.8384
3.7	2.28	0.001095	0.009524	205.62	223.85	429.47	1.0196	0.8128	1.8324
3.8	3.31	0.001103	0.009215	208.19	220.57	428.76	1.0286	0.7978	1.8264
3.9	4.31	0.001111	0.008921	210.74	217.28	428.02	1.0374	0.7830	1.8204
4	5.30	0.001119	0.008640	213.27	213.98	427.25	1.0461	0.7684	1.8145
4.1	6.27	0.001127	0.008372	215.78	210.66	426.44	1.0547	0.7539	1.8086
4.2	7.22	0.001135	0.008114	218.28	207.33	425.61	1.0632	0.7395	1.8027
4.3	8.16	0.001144	0.007868	220.75	203.99	424.74	1.0716	0.7251	1.7967

Figure 8. Database

6. Conclusion

The objective of the project is achieved. But the source of the data is limited. So, the database is only limit for the certain number. This is the main problem actually. All the data of properties should be calculated. Enthalpy and entropy should be count with a proven source of data like internal energy, U. The database will be more interesting if it have full model of performance calculation including P-h (Pressure-enthalpy) and T-s (Temperature-entropy) diagram. A suitable format should be organized for evaluating refrigerant and heat pumps system.

The source of database is limited. Such as, for the superheated vapor, the range temperature is within -10 until 170 and 10 until 200 (in Celsius). All those data are from reported and published source. But, maybe due to privacy they do not separated all the values.

With the development of technology nowadays, more software has come out and more attractive database has been done from many organizations and researchers. Therefore, there are many aspects should be improved in order to obtain an enhancement on the database in the future.

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