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S. Fischer

Oak Ridge National Laboratory

J. Sand

Oak Ridge National Laboratory

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THERMODYNAMIC CALCULATIONS FOR MIXTURES
OF ENVIRONMENTALLY SAFE REFRIGERANTS
USING THE LEE-KESLER-PLÖCKER EQUATION OF STATE

Steven Fischer and Jim Sand
Oak Ridge National Laboratory

ABSTRACT

The imminent phaseout of R-11, R-12, and R-115 because of their high ozone depletion potentials has prompted many independent investigations of alternative or substitute refrigerants, either as pure compounds or as mixtures of two or more environmentally acceptable fluids. There are several motivations for investigating mixtures. There are very few pure compounds which can be used for refrigerants that are non-toxic, non-flammable, and also have very low ozone depleting potentials (ODP) and greenhouse warming potentials (GWP). Mixtures composed of three or more components offer a distinct advantage in that careful selection of the components could permit a flammable refrigerant to be used in a blend that remains non-flammable under all conceivable conditions. Also, component concentrations in ternary or higher order mixtures can be adjusted to linearize the temperature-enthalpy profile of a mixture making it more suitable for applications where secondary fluids are heated or cooled through large temperature glides (i.e., refrigeration and air conditioning).

The computer model LKPSIM was constructed from subroutines written by Ulf Plöcker and incorporated into a Lorenz cycle refrigerator/freezer simulation model for binary refrigerant mixtures developed at the University of Hannover. Modifications were made to the Hannover routines to compute thermodynamic properties for mixtures of three or more components, the list of available refrigerants was expanded from 11 to 17 possible choices, and a new correlation was developed for computing the interaction coefficients for mixtures of halocarbon refrigerants. Tables of refrigerant molecular weights, critical temperatures and pressures, normal boiling points, acentric factors, and coefficients for fits to the ideal gas heat capacity for each refrigerant are built into a menu-driven data input routine for ease of use.

Results of calculations of saturated and superheated vapor properties from the LKPSIM program were compared with experimental data and with computations using the Carnahan-Starling-DeSantis (CSD) equation of state (EOS) for pure refrigerants and for binary and ternary mixtures of refrigerants. There is excellent agreement between the calculations and the published data for pure refrigerants that are well characterized (e.g., R-12, R-22) with greater discrepancies between LKPSIM and data from other sources for newer compounds (e.g., R-143a, R-124). Calculations were also performed to validate the program for mixtures. LKPSIM calculations agreed more closely with observed saturation properties for mixtures of R-143a and R-124 over a range of operating conditions and mixture compositions than did those of the CSD EOS. It also gave very close agreement with data from a manufacturer of a ternary blend of refrigerants.

The CYCLE-7 program from the National Institute of Standards and Technology (NIST) was adapted to use the LKP subroutines with mixtures of three or more components (McLinden). CYCLE-7 is a thermodynamic model for a Rankine cycle with counterflow heat exchangers using specified pressure drops and log mean ΔT 's for the condenser and evaporator. The modified program (CYCLE-10) was tested against known sets of data for pure refrigerants and blends of two and three components and will be used in screening tests of blends of fluids with low ODPs and GWPs for applications in heat pumps and refrigerating equipment.

INTRODUCTION

Environmental concerns have prompted an international effort by private industry and government laboratories to identify new compounds that can be used as refrigerants which do not pose a threat to stratospheric ozone and would not contribute to global warming. The search for new refrigerants has led to extensive investigations of pure compounds that could be used in refrigeration systems (McLinden 1987). Work is also being done on combining fluids to form mixtures of two and three compounds (Bivens, 1989 and Vineyard, 1989). The tremendous number of combinations of fluids that could be used in a mixture requires that models be used to screen the alternatives analytically and that only the most promising blends be examined in the laboratory.

Equations-of-state (EOS) are used to estimate the enthalpy, entropy, density, and specific volume of liquid and vapor under saturated, subcooled, and superheated conditions. The Carnahan-Starling-DeSantis (CSD), Benedict-Webb-Rubin (BWR), Peng-Robinson, Lee-Kesler-Plöcker (LKP), and Redlich-Kwong-Soave (RKS) models are all used for these purposes and each has its advantages and disadvantages (Gerdsmeier, 1988). One advantage the LKP EOS has in the screening of components for mixtures is that it does not require an extensive body of experimental data to give accurate results. The LKP equation of state requires data for the critical temperature, pressure, and molar volume of each component in the mixture, molecular weights, normal boiling points, and correlations for ideal gas heat capacities as functions of the absolute temperature (actually the difference between the desired temperature and a reference temperature). The LKP EOS also uses an acentric factor for each component which can be specified from experimental data or computed from the critical properties of that compound.

The LKP EOS is a corresponding states model which relates the properties of a fluid to its critical temperature, pressure, and volume, its molecular weight, and to a few other fundamental properties. The CSD and RKS equations of state are based on a hard sphere theory of molecular structure, and while they give very good results for pure fluids they require experimental data on the interaction of the compounds when they are applied to mixtures. This requirement for experimentally determined interaction coefficients makes it difficult to estimate thermodynamic properties for mixtures using some of the newer compounds. The LKP method can be used more easily for new compounds because Plöcker developed a computer correlation to supply this parameter.

One of the refinements that Plöcker made to the work of Lee and Kesler was to correlate the interaction coefficients for a large number of binary systems to the critical temperatures and molar volumes of the two components (Plöcker, 1978 and Plöcker, 1977). Figure 1 shows Plöcker's correlation for the interaction coefficients for hydrocarbon-hydrocarbon mixtures (solid line) and the experimental data points that he used to generate this curve. His correlation works very well in predicting the thermodynamic properties of mixtures of halocarbon refrigerants in the absence of experimentally determined interaction coefficients (both the LKP and CSD models are always more accurate when experimentally determined interaction coefficients are available). Consequently computer routines based on the LKP EOS could be valuable for evaluating mixtures of new compounds in the effort to find environmentally safe blends of refrigerants for use as alternatives to R-12 and R-502.

APPROACH

A computer program was obtained from M. Kauffeld and H. Kruse of the University of Hannover, Federal Republic of Germany which used Plöcker's subroutines to simulate the performance of a refrigerator/freezer using the Lorenz cycle with a binary mixture of refrigerants (Kauffeld 1989). The subroutines for the thermodynamic calculations were extracted from this program and modified so they could be used for mixtures with more than two components.

Further changes were made so the program would be more accurate for mixtures of halocarbon refrigerants. Figure 1 includes data used to develop the interaction coefficient correlation for a large set of hydrocarbons with high molecular weights. A subset of this information was chosen which included only the mixtures of compounds that are similar in molecular structure and weight to the halocarbon refrigerants.

Interaction coefficients that Kruse and Kauffeld added to Plöcker's subroutines were also included in this set and then a curve was fit to these data and the corresponding equation was incorporated into the code.

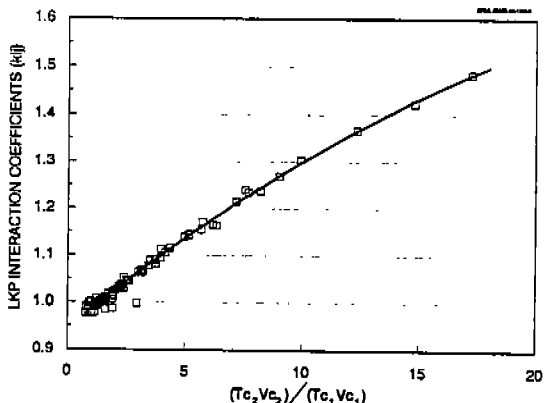


Fig 1. Interaction coefficients for binary mixtures of hydrocarbon-hydrocarbon systems.

The original code allowed the user to choose from a list of 11 possible refrigerants (R-11, R-12, R-13, R-13B1, R-14, R-22, R-23, R-113, R-114, R-152a, and R-142b). Properties were added to the subroutines for six additional refrigerants (R-32, R-115, R-123, R-124, R-134a, and R-143a). The LKP subroutines can be modified to include additional refrigerants by providing:

- the critical temperature, pressure, and molar volume,
- the molecular weight,
- the normal boiling point (only used to sort the components by volatility and to compute an acentric factor for the fluid if one is not specified), and
- a function for the ideal gas heat capacity, C_p^0 . Typically the ideal gas heat capacity is given by an equation such as:

$$C_p^0(T) = a_1 + a_2T + a_3T^2 + a_4T^3 + \frac{a_5}{T} \quad (1)$$

It is also helpful to be able to provide a correlation for the saturation temperature as a function of the pressure. If C_p^0 is given by Eq. 1, then enthalpy and entropy departure functions $H^0(T, T_{Ref})$ and $S^0(T, T_{Ref})$ are given by:

$$H^o(T, T_{Ref}) = \int_{T_{Ref}}^T C_p^o(\tau) d\tau = a_1(T - T_{Ref}) + \frac{a_2}{2} (T^2 - T_{Ref}^2) + \quad (2)$$

$$\frac{a_3}{3} (T^3 - T_{Ref}^3) + \frac{a_4}{4} (T^4 - T_{Ref}^4) + a_5 \ln\left(\frac{T}{T_{Ref}}\right)$$

and

$$S^o(T, T_{Ref}) = \int_{T_{Ref}}^T \left(C_p^o(\tau)/\tau \right) d\tau = a_1 \ln\left(\frac{T}{T_{Ref}}\right) + a_2(T - T_{Ref}) + \frac{a_3}{2} (T^2 - T_{Ref}^2) + \quad (3)$$

$$\frac{a_4}{4} (T^3 - T_{Ref}^3) - a_5 \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right).$$

These modified subroutines were incorporated into a program named LKPSIM¹ which provides convenient menu driven input for selecting refrigerants, the type of calculation to be performed, a choice of units between SI and English units, and a printer setup routine. LKPSIM allows the user to choose between evaluating liquid and vapor saturation properties for a single specified temperature or pressure or to generate a table of saturation properties for a range of temperatures. Other options permit the user to compute the properties of superheated vapor at a single condition, to generate tables of superheat data, or to calculate the performance of an ideal vapor compression cycle for specified condensing and evaporating temperatures and superheat and subcooling conditions.

RESULTS

For validation, LKPSIM was used to compute tables of data for pure refrigerants and binary and ternary mixtures of refrigerants. Table 1 shows a comparison between the results of the LKP calculations and data published by ASHRAE (1989) for saturated R-12 liquid and vapor. Similar results were obtained for R-22.

Comparisons were also made for azeotropic and nonazeotropic binary mixtures of refrigerants. The solid lines in Fig. 2 show the saturated liquid and vapor enthalpies for R-502 (an azeotrope of R-22 and R-115) that were computed using LKPSIM and the discrete points published by ASHRAE (1989). There is good agreement between these sets of data, though not as good as that for R-12 with differences ranging from -1.39 to 3.87 kJ/kg for saturated liquid and -9.23 to -11.79 kJ/kg for the vapor. Table 2 presents a comparison of data from LKPSIM and routines using the CSD equation of state for nonazeotropic mixtures of R-143a and R-124. Laboratory tests with these blends in a breadboard heat pump system rig were controlled to give wet vapor leaving the evaporator (no superheat). When experimentally measured temperatures and pressures from the breadboard rig are used with the CSD and LKP routines to calculate the state of the refrigerant leaving the evaporator, the LKP results show lower superheat than those computed using the CSD routines. Figure 3 shows the enthalpies of saturated liquid and vapor for a blend of R-22, R-152a, and R-124 where the solid lines again represent the data computed using the Lee-Kesler-Plöcker equation of state and where the discrete points show the data provided by one of the refrigerant manufacturers (Bivens, 1989). The agreement is actually better for this ternary blend than it is for R-502.

The enthalpy of superheated vapor for a ternary blend are shown in Fig. 4 at 0.069 MPa and 2.413 MPa and the differences range from -0.6 to +2.8%. This agreement is not as close as desired and further work is planned to resolve this discrepancy.

¹ written in Microsoft QuickBasic for use on IBM PC compatible computers.

TABLE 1. SATURATION PROPERTIES FOR R-12 FROM LKPSIM AND ASHRAE TABLES

TEMPERATURE (°C)	ENTHALPY OF LIQUID			ENTHALPY OF VAPOR		
	LKP	ASHRAE	DEVIATION	LKP	ASHRAE	DEVIATION
	(kJ/kg)	(kJ/kg)	(kJ/kg)	(kJ/kg)	(kJ/kg)	(kJ/kg)
-80.	128.85	129.59	0.74	536.46	537.07	0.61
-60.	145.95	146.58	0.63	545.89	546.40	0.51
-40.	163.53	163.86	0.33	555.33	555.77	0.44
-20.	181.54	181.61	0.07	564.58	565.01	0.43
0.	200.00	200.00	0.00	573.40	573.91	0.51
20.	219.00	219.18	0.18	581.52	582.21	0.69
40.	238.73	239.29	0.56	588.58	589.49	0.91
60.	259.51	260.58	1.07	593.32	595.02	1.70
80.	282.10	283.70	1.60	596.07	597.20	1.13

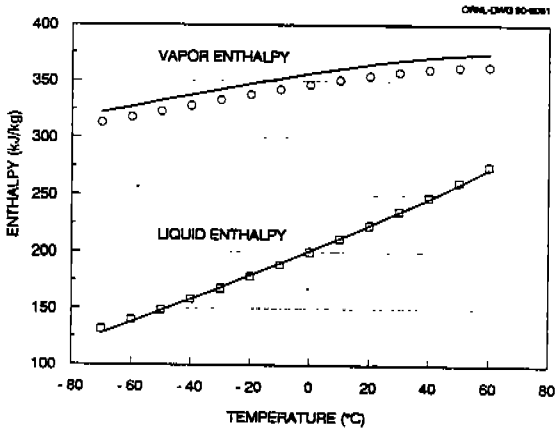


Fig. 2. Enthalpy of saturated R-502 computed using LKP equation of state (solid lines) and data published by ASHRAE (discrete points).

TABLE 2. CALCULATED SUPERHEATS USING LKP AND CSD MODELS AT LABORATORY CONDITIONS

TEST NUMBER	FRACTION R-143a	FRACTION R-124	PRESSURE (kPa)	TEMPERATURE (°C)	EVAPORATOR SUPERHEAT	
					LKP (°C)	CSD (°C)
1.	0.33	0.67	353	12.0	1.8	3.0
2.	0.33	0.67	381	14.7	2.2	3.3
3.	0.64	0.36	543	13.4	2.2	3.4
4.	0.64	0.36	559	14.4	2.2	3.5
5.	0.64	0.36	596	17.9	3.7	4.9
6.	0.77	0.23	599	11.8	2.8	3.9
7.	0.77	0.23	639	14.0	2.9	3.9
8.	0.77	0.23	656	16.9	5.1	6.1
9.	0.77	0.23	682	16.1	2.9	3.8

CYCLE ANALYSES

The LKP subroutines have been developed to provide tools for evaluating refrigerant mixtures and identifying the acceptable blends which promise to perform best in refrigerating equipment. Although the thermodynamic properties calculated with LKPSIM can be used to compute theoretical cycle efficiencies, the most useful analytical results would take into account some of the non-ideal conditions in real equipment. This is particularly important for comparing mixtures of refrigerants. CYCLE-7 (McLinden, 1985) is a system simulation model developed at the National Institute of Standards and Technology (NIST) which incorporates heat exchanger pressure drops and uses an LMTD method for heat exchanger loading. A copy of the source code for CYCLE-7 for binary mixtures was obtained from NIST and modified to use the LKP subroutines for ternary and higher order mixtures.

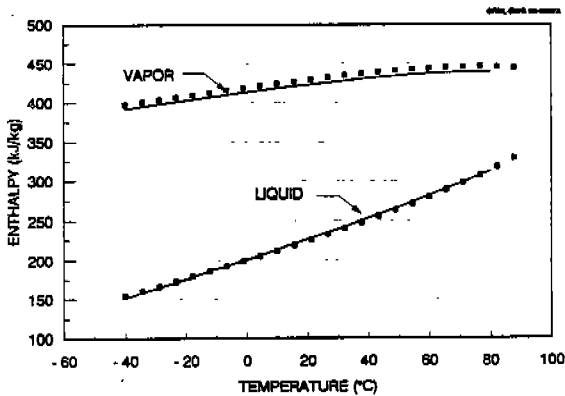


Fig. 3. Comparison of liquid and vapor enthalpies for a mixture of R-22, R-152a, and R-124.

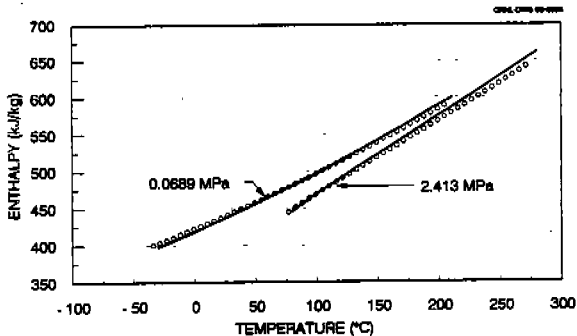


Fig. 4. Comparison of enthalpy of superheated vapor computed using the LKP EOS (solid lines) and data from the manufacturer for a mixture of R-22, R-152a, and R-124.

The modified code, CYCLE-10, is written for use on IBM PC's and PC-compatible computers and includes an interactive subroutine for data input. The user is required to specify:

1. the number of components in the mixture (maximum of 4),
2. each component by name (cursor keys are used to select from the list of available refrigerants),
3. the mass fraction of each component in the mixture,
4. the log mean temperature difference (LMTD) for each heat exchanger,
5. the pressure drop in each heat exchanger,
6. the compressor isentropic efficiency, and
7. the secondary fluid temperatures entering and leaving each heat exchanger.

Default values are built into the program for each of these parameters so they do not all have to be specified, and values are "sticky" in the sense that the numbers entered by the user continue to be used from one set of calculations to the next until they are changed. The iterative loops in the program can be somewhat time consuming so intermediate results are displayed on the screen so the user can monitor the progress of the calculations.

The printed output from a typical run of CYCLE-10 is shown in Fig. 5 for a ternary blend of refrigerants under typical conditions for a refrigerator/freezer. This listing gives a complete summary of the input data and the calculated refrigerant capacities, temperature glides, COPs, compressor discharge temperature, discharge superheat, and pressure ratio. A table of the thermodynamic properties and refrigerant composition at each of five state points in the cycle is printed at the bottom of the output.

FUTURE WORK

Slight modifications will be made to the model to simulate the operating features of a commercial refrigeration system and the revised CYCLE-10 program will be used to screen a broad list of refrigerant mixtures to identify blends which have the potential of being environmentally acceptable alternatives to R-502 and R-12. Refrigerants that are likely candidates as components of mixtures in these analyses are R-32, R-124, R-125, R-134, R-152a, R-134a, and R-143a. CYCLE-10 will be run exhaustively for combinations of these compounds in binary and ternary blends and the results will be examined for high COP and acceptable discharge temperatures, pressure ratios, and volumetric capacity (data on flammability and "composite" ODP and GWP will be used in evaluating the results from the cycle model).

Preliminary work has been done on this screening analysis and the calculated COPs for ternary blends of R-22, R-152a, and R-124 are shown in Fig. 6. The percentage (mass fraction) of each compound in the mixture is varied from 0% to 100% in 10% increments. The top of each column is labeled with the concentration of R-152a, each row is labeled on the right with the percentage of R-22 in the mixture, and each diagonal is labeled on the left with the fraction of R-124. Thus a refrigeration cycle using pure R-152a would have a COP of 1.35 (top right corner) for the conditions summarized at the bottom of this figure, pure R-22 a COP of 1.40 (bottom square), and pure R-124 a COP of 1.15 (top left). Each column shows a constant percentage of R-152a, so the COP of solutions with 50% R-152a would increase from 1.292 to 1.394 as the percentage of R-22 is increased from 0% to 50% (and R-124 decreases from 50% to 0%). Likewise each row represents a fixed percentage of R-22 and each diagonal a fixed percentage of R-124. Figure 6 also contains shaded areas that indicate the mixture compositions that are flammable and compositions that have excessive discharge temperatures (theoretical discharge temperatures above 118°C). Thus the maximum COP for non-flammable mixtures with "acceptable" discharge temperatures is about 1.35 with a composition around 40% R-124, 35% R-22, and 25% R-152a (depending on how close the composition can be to the flammable region, variations of isentropic efficiency with pressure ratio, etc.).

These screening analyses are just beginning and it is too early to draw any conclusions from results obtained thus far. However, we expect that LKPSIM and CYCLE-10 will be valuable and convenient tools that can reduce the amount of future laboratory effort in the screening and selection of alternative refrigerant blends.

REFRIGERANTS:	MASS FRACTION	MOLE FRACTION
1. R-22	40.0%	38.1%
2. R-124	20.0%	12.1%
3. R-152a	40.0%	49.9%
INPUT DATA	EVAPORATOR	CONDENSER
Secondary Fluid Temperatures:		
into heat exchanger	34.7 C	-17.1 C
out of heat exchanger	31.9 C	-22.1 C
Log Mean Temperature Difference	10.0 C	12.0 C
Pressure Drop	13.7 kPa	13.7 kPa
Isentropic Compressor Efficiency	55.0%	
CALCULATED RESULTS	REFRIGERATION	HEATING
ODP	1.369	2.369
Work Input	120.8 kJ/kg	120.8 kJ/kg
Refrigerant Capacity	165.4 kJ/kg	286.1 kJ/kg
Volumetric Capacity	621.5 kJ/m ³	1,075.4 kJ/m ³
Temperature Glide	-1.24 C	2.72 C
COMPRESSOR:		
Discharge Superheat	80.8 C	
Discharge Temperature	120.7 C	
Pressure Ratio	11.6	

State Point	Temperature (C)	Pressure (kPa)	Enthalpy (kJ/kg)	Volume (m ³ /kg)	Entropy (kJ/kg C)	Vapor Quality	Mass Fraction		
							Liquid	Vapor	
1. Compressor Inlet	-30.6	89.1	273.778	0.266	1.23280	1.000	0.254	0.400	R-22
							0.322	0.200	R-124
							0.444	0.400	R-152a
2. Compressor Discharge	120.7	1,028.7	394.542	0.036	1.38054	1.408	*****	0.400	R-22
							*****	0.200	R-124
							*****	0.400	R-152a
3. Condenser Saturation	39.9	1,024.7	311.848	0.025	1.14435	1.000	0.298	0.400	R-22
							0.272	0.200	R-124
							0.430	0.400	R-152a
4. Condenser Outlet	37.2	1,015.0	108.404	0.001	0.39620	0.000	0.400	0.514	R-22
							0.200	0.138	R-124
							0.400	0.348	R-152a
5. Evaporator Inlet	-29.4	102.8	108.404	0.085	0.48068	0.360	0.333	0.519	R-22
							0.237	0.135	R-124
							0.430	0.346	R-152a

Fig. 5. Sample output from CYCLE-10 for a ternary blend of refrigerants.

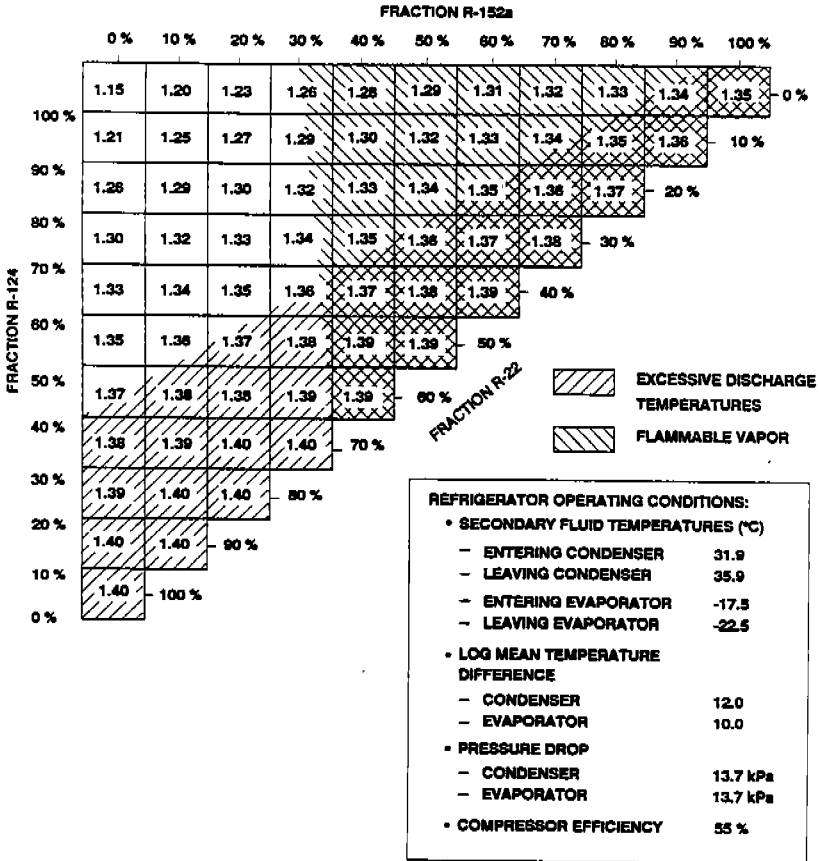


Fig. 6. Refrigerating COPs for ternary mixtures of R-152a, R-22, and R-124.

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