

Application of Procedures to Calculate Thermodynamic Properties of Carbon Dioxide, HFC-134a and HCFC-22

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ABSTRACT: Systematic methods to calculate thermodynamic properties of carbon dioxide, HFC-134a and HCFC-22 are presented. First, application of a basic method to identify the saturation state with given temperature or pressure is attempted and the feasibility of auxiliary equations is tested. Next, detailed procedures are suggested to tell a phase when temperature/pressure and another property are specified. Finally the Newton-Raphson method is applied to calculate unknown thermodynamic properties fixing the state with the two independent properties specified. The procedures described here are utilized to develop a computer program, which is used to find the relation between temperature and pressure with maximum isobaric heat capacity for super-critical carbon dioxide.

Nomenclature

a : Helmholtz function [kJ/kg]
 C_p : constant-pressure specific heat [kJ/kg K]
 C_v : constant-volume specific heat [kJ/kg K]
 g : Gibbs function [kJ/kg]
 GWP : global warming potential
 h : enthalpy [kJ/kg]
 NBP : normal boiling point
 ODP : ozone depletion potential
 P : pressure [kPa]
 R : gas constant [kJ/kg K]
 s : entropy [kJ/kg K]
 T : temperature [K]
 u : internal energy [kJ/kg]

v : specific volume [m^3/kg]
 w : speed of sound [m/s]

Greek symbols

ϕ : non-dimensional Helmholtz function
 ρ : density [kg/m^3]
 δ : reduced density ($= \rho/\rho_c$)
 τ : inverse of reduced temperature ($= T_c/T$)
 μ_J : Joule-Thomson coefficient [K/kPa]

Superscripts

0 : ideal gas Helmholtz function
 r : residual Helmholtz function

Subscripts

c : critical point
 f : saturated liquid state
 g : saturated vapor state

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- n : number of iterations
 r : reduced property
 s : saturation state

1. Introduction

Thermal system design requires understanding of thermodynamic characteristics and calculation of thermodynamic properties. For this calculation, it is necessary to have ideal gas specific heats and the equation of state which are determined based on a large amount of experimental data obtained by several long-term precise measurements. Preferred equation of state is expected to well represent the behavior of a substance in a vapor state and in a liquid state as well so that such an equation tends to be in a quite complicated form. This makes it almost impossible to make hand calculation of properties. Instead it is a usual practice to evaluate the properties on a computer. This practice invokes the development of appropriate computer programs.

Existing programs related to the foregoing practice are: H2OCALC⁽¹⁾ which reproduces ASME steam tables, PROPATH⁽²⁾ of Kyushu University in Japan, ALLPROP⁽³⁾ of Idaho University and NIST REFPROP⁽⁴⁾ developed to calculate mainly the properties of mixture refrigerants. H2OTAB and CO2TAB⁽⁵⁾ are spreadsheet type programs. NIST Webbook⁽⁶⁾ is an on-line property database on the web.

These various computer programs abroad compare domestic ones hardly found as far as the

authors can tell. The situation initiated this study to review systematic procedures for the calculation of the unknown properties with two given property values and then to develop computer programs. Application will also be made to find out the relation between temperature and pressure at which the constant-pressure specific heat of CO₂ becomes a maximum.

2. Equations of state

In this study, we deal with CO₂, HFC-134a and HCFC-22 for which equations of state are selected to be reliable and most up-to-date in the literature, Span and Wagner,⁽⁷⁾ Tillner-Roth and Baehr⁽⁸⁾ and Kamei et al.,⁽⁹⁾ respectively. The equations are provided in terms of the reduced Helmholtz function.

$$\phi = \frac{a}{RT} \quad (1)$$

where $a = u - Ts$. The Helmholtz function can be used to derive all the thermodynamic properties by differentiations and simple algebraic manipulations so that preciseness and thermodynamic consistency are reserved.⁽¹⁰⁾ On the other hand, direct use of an equation of state and ideal gas specific heats for the derivation of properties requires integrations from which difficulties of the appearance of constants may arise. The term $\phi(\delta, \tau)$ in equation (1) is separated into an ideal gas term, $\phi^0(\delta, \tau)$ and a residual term, $\phi^r(\delta, \tau)$, or

Table 1 Summary on the equations of state

	Carbon dioxide	HFC-134a	HCFC-22
Equation of state	Span & Wagner (1996)	Tillner-Roth & Baehr (1994)	Kamei et al. (1995)
Temperature range (K)	216~1100	170~455	200~550
Pressure range (MPa)	0~800	0~70	0~60
Uncertainties	Density 0.03~0.05%	Density 0.05%	Density 0.1%
	Speed of sound 0.03~1%	Vapor pressure 0.02%	Speed of sound 0.1%
	Heat capacity 0.15~1.5%	Heat capacity 0.5~1.0%	Heat capacity 0.5%

Table 2 Characteristic data for carbon dioxide, HFC-134a and HCFC-22

Property / Index		Carbon dioxide	HFC-134a	HCFC-22
Chemical formula		CO ₂	CF ₃ -CH ₂ F	CHClF ₂
Molecular weight		44.0098 kg/kmol	102.032 kg/kmol	86.469 kg/kmol
Gas constant		0.188924 kJ/kg·K	0.0814889 kJ/kg·K	0.096156 kJ/kg·K
Critical point	Temperature	304.1282 K	374.21 K	369.295 K
	Pressure	7.3773 MPa	4.0593 MPa	4.990 MPa
	Density	467.6 kg/m ³	511.95 kg/m ³	523.85 kg/m ³
Triple point	Temperature	216.592 K	169.85 K	115.73 K
	Pressure	0.51795 MPa	0.391 kPa	0.37904 Pa
Others	NBP	194.65 K	225.92 K	232.34 K
	GWP	1	1300	1700
	ODP	0	0	0.05

$$\phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^r(\delta, \tau) \quad (2)$$

$$I \equiv \int_f^g v dP \quad (5)$$

where $\delta = \rho/\rho_c$, $\tau = T_c/T$ and ρ , T , ρ_c , and T_c are density, absolute temperature, critical density, and critical temperature, respectively. More detailed discussions on $\phi^0(\delta, \tau)$ and $\phi^r(\delta, \tau)$ are given in the literature.⁽⁷⁻⁹⁾ Table 1 shows applicable ranges and estimated uncertainties. Characteristic values for the 3 substances are listed in Table 2.

Then

$$I = g_g - g_f = - \int_f^g (P - P_s) dv = 0 \quad (6)$$

where P_s is a saturation pressure at T . If we replace P_s with an arbitrary one, P_x , then

$$I = (P_x - P_s)(v_g - v_f) \neq 0 \quad (7)$$

3. Determination of saturation state

3.1 With given saturation temperature

The saturation state at a given temperature can be determined using the Gibbs function condition. In a saturation state Gibbs function for the liquid, g_f is equal to the Gibbs function for the vapor, g_g ; i.e.,

$$g_f = g_g \quad (3)$$

By definition,

$$g_g - g_f = \int_f^g v dP = 0 \quad (4)$$

Therefore, we introduce

where v_g is a specific vapor-like volume and v_f is a specific liquid-like volume at (T, P_x) .

Equations (6) and (7) can be used, by iteration, to determine the saturation pressure at a given temperature keeping thermodynamic consistency but requiring longer computer time, which becomes a shortcoming. To avoid this, provided are the auxiliary equations for saturated liquid density, saturated vapor density and vapor pressures along with the Helmholtz functions.^(7,8,11) Use of the auxiliary equations reduces computer time losing thermodynamic consistency to some extent so that we have to examine the accuracies of the auxiliary equations.

Comparing saturation pressures calculated from

the Helmholtz function with those calculated using vapor pressure equations recommended yielded 0.002% of errors for CO₂ and 0.01% for HCFC-22, very small deviations. This led that we may use the recommended vapor pressure equations as is. Saturated density correlations also gave reasonable maximum deviations of 1.0% or so. These equations, therefore, are used to provide initial values for various iterative calculations. For HFC-134a,⁽⁸⁾ saturated liquid density correlation was reliable with a maximum deviation as small as 0.2%. However, other deviations were not negligible (maximum of 1.7% for vapor pressures, 4.1% for saturated vapor densities). Consequently, we decided to develop alternative correlations of our own.

In this study, vapor pressure correlation is used not to reproduce real experimental data but to faithfully represent the vapor pressures obtained from the Helmholtz function. For HFC-134a, vapor pressure 'data' at various temperatures are generated from the Helmholtz function; then the data are fitted to the following correlation:⁽¹²⁾

$$\ln P_s/P_c = b_1\beta + b_2\beta^{1.5} + b_3\beta^2 + b_4\beta^{3.5} \quad (8)$$

where $\beta = \tau - 1$, P_c being a critical pressure. In a similar manner, a saturated vapor density equation⁽¹³⁾ is obtained as

Table 3 Coefficients of auxiliary equations

Coefficient	Value	Note
b_1	-7.686556	Eq. (8)
b_2	2.311791	
b_3	-2.039554	
b_4	-3.583758	
c_1	-2.0043	Eq. (9)
c_2	-4.0986	
c_3	1.0277	
c_4	-2.4757	
c_5	0.62373	

$$\ln \rho_g/\rho_c = c_1\beta^{1/3} + c_2\beta^{2/3} + c_3\beta^{1/2} + c_4\beta^{1.5} + c_5\beta^2 \quad (9)$$

Table 3 shows the coefficients in Eqs. (8) and (9). The new correlations yield maximum deviations of 0.025% and 0.5% for vapor pressures and saturated vapor densities, respectively, showing better reproduction than the original auxiliary correlations.

3.2 With given saturation pressure

Saturation temperature at a given saturation pressure can be determined by Newton-Raphson method as

$$T_{n+1} = T_n - \frac{P_s(T_n) - P_s}{dP_s/dT} \quad (10)$$

where n is the number of iteration, dP_s/dT is evaluated using a saturation pressure correlation. Then similar procedure in section 3.1 is followed for the rest of calculations.

4. Property calculation with given T

4.1 With given T and v

First, when the temperature is higher than the critical, pressure can be determined using the Helmholtz function as

$$P = \rho RT(1 + \delta\phi_\delta^r) \quad (11)$$

where R is a gas constant and $\phi_\delta^r = \partial\phi^r/\partial\delta$. Other properties can be obtained as

$$h = RT[1 + \tau(\phi_\tau^o - \phi_\tau^r) + \delta\phi_\delta^r] \quad (12)$$

$$s = R[\tau(\phi_\tau^o + \phi_\tau^r) - \phi^o - \phi^r] \quad (13)$$

$$u = h - Pv \quad (14)$$

$$g = h - Ts = a + Pv \quad (15)$$

$$C_v = -R\tau^2(\phi_{\tau\tau}^o - \phi_{\tau\tau}^r) \quad (16)$$

$$C_P = C_v - T[(\partial P/\partial T)_v]^2/(\partial P/\partial v)_T \quad (17)$$

$$w = v\sqrt{T/C_v(\partial P/\partial T)_v^2 - \partial P/\partial v}_T \quad (18)$$

$$\mu_J = \frac{v(\partial P/\partial v)_T + T(\partial P/\partial T)_v}{T(\partial P/\partial T)_v^2 - C_v(\partial P/\partial v)_T} \quad (19)$$

$$\partial P/\partial v)_T = -\rho^2(\partial P/\partial \rho)_T \quad (20)$$

$$\partial P/\partial \rho)_T = RT(1 + 2\delta\phi_\delta^r - \delta^2\phi_{\delta\delta}^r) \quad (21)$$

$$\partial P/\partial T)_v = \rho R(1 + \delta\phi_\delta^r - \delta\tau\phi_{\delta\tau}^r) \quad (22)$$

where $\phi_\tau^0 = \partial\phi^0/\partial\tau)_\delta$, $\phi_\tau^r = \partial\phi^r/\partial\tau)_\delta$, $\phi_\delta^0 = \partial\phi^0/\partial\delta)_\tau$, $\phi_{\tau\tau}^0 = \partial^2\phi^0/\partial\tau^2)_\delta$, $\phi_{\tau\tau}^r = \partial^2\phi^r/\partial\tau^2)_\delta$ and $\phi_{\delta\delta}^r = \partial^2\phi^r/\partial\delta^2)_\tau$. Reference state is a saturated liquid at 273.15 K where assigned values of h and s are 200 kJ/kg and 1 kJ/kgK, respectively. Above the critical temperature, there is a minimum value of specific volume, $v_{P_{\max}}$ at a maximum pressure, P_{\max} (up to which the equation of state is applicable) as shown in the $P-v$ diagram of Fig. 1. The minimum volume, $v_{P_{\max}}$ is fitted to the data appears in the property tables⁽⁷⁻⁹⁾ as

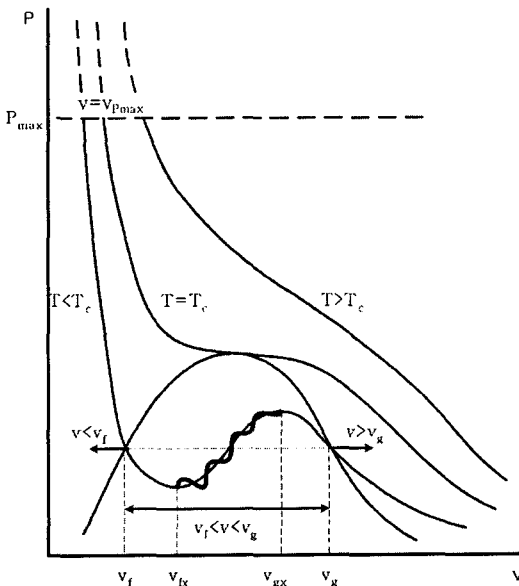


Fig. 1 $P-v$ diagram.

Table 4 Coefficients of Eq. (23)

Substance	Coefficient		
	A	B	C
Carbon dioxide	1773.11	-0.96148	3.16110e-4
HFC-134a	2034.95	-2.34027	7.33299e-4
HCFC-22	1901.23	-1.83736	0

$$v_{P_{\max}} = A + BT + CT^2 \quad (23)$$

where the values of A , B , C are in Table 4.

Below the critical temperature, properties are calculated after the phase is determined as:

- (1) If $v < v_f$ then (compressed) liquid phase,
- (2) If $v > v_g$ then (superheated) vapor phase,
- (3) If $v_f \leq v \leq v_g$ then two phase.

Compressed liquid should satisfy the inequality, $v \geq v_{P_{\max}}$. The quality, $x = (v - v_f)/v_{fg}$ for the saturation state.

4.2 With given T and P

First, regions in the $P-T$ diagram (Fig. 2) are classified as supercritical (I), superheated

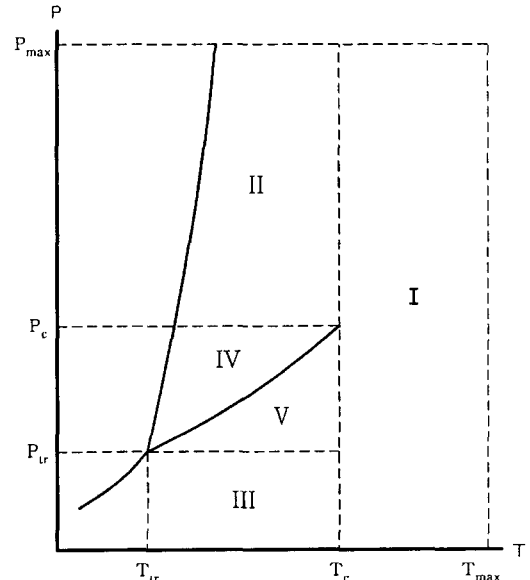


Fig. 2 $P-T$ diagram.

vapor (III, V) and compressed liquid (II, IV). Phase and the interval of specific volume are fixed depending on the values of temperature and pressure. Then, within the interval of search, specific volume is determined using Newton-Raphson method as

$$v_{n+1} = v_n - \frac{P(T, v_n) - P}{\partial P / \partial v)_T} \quad (24)$$

where n is the number of iteration and $\partial P / \partial v)_T$ is evaluated by Eqs. (20) and (21).

4.3 With given T and s

In this case, specific volume is adjusted so that the calculated entropy at (T, v) be the same as the given one. Phase and the interval of specific volume are fixed depending on the values of temperature and entropy. Compressed liquid should satisfy the inequality, $s \geq s_{P_{\max}}$ where $s_{P_{\max}}$ is the entropy of compressed liquid at a maximum pressure, P_{\max} in Table 1 or a melting pressure. The quality, $x = (s - s_f) / s_{fg}$ for the saturation state.

Then, within the interval of search, specific volume is determined using Newton-Raphson method as

$$v_{n+1} = v_n - \frac{s(T, v_n) - s}{\partial s / \partial v)_T} \quad (25)$$

where $\partial s / \partial v)_T = \partial P / \partial T)_v$, the Maxwell relation and $\partial P / \partial T)_v$ is evaluated by Eq. (22).

5. Property calculation with given P

5.1 With given P and v

First, at (T_c, P) , specific volume, v_x is calculated. Then phase and the interval of temperature are fixed depending on the values of

pressure and specific volume. The quality, $x = (v - v_f) / v_{fg}$ for the saturation state. Within the interval of search, temperature is determined using Newton-Raphson method as

$$T_{n+1} = T_n - \frac{v(T_n, P) - v}{\partial v / \partial T)_P} \quad (26)$$

where

$$\partial v / \partial T)_P = - \frac{\partial P / \partial T)_v}{\partial P / \partial v)_T} \quad (27)$$

and $\partial P / \partial v)_T$ and $\partial P / \partial T)_v$ are evaluated by Eqs. (20), (21) and (22).

5.2 With given P and h

In this case, temperature is adjusted so that the calculated enthalpy at (T, P) be the same as the given one. First, enthalpy, h_x at (T_c, P) is calculated. Then phase and the interval of temperature are fixed depending on the values of pressure and enthalpy. Within the interval of search, temperature is determined using Newton-Raphson method as

$$T_{n+1} = T_n - \frac{h(T_n, P) - h}{\partial h / \partial T)_P} \quad (28)$$

where $\partial h / \partial T)_P = C_P$ and C_P is evaluated by Eq. (17).

5.3 With given P and s

In a similar manner to the section 5.1, temperature is adjusted so that the calculated entropy at (T, P) be the same as the given one. Within the interval of search, temperature is determined using Newton-Raphson method as

$$T_{n+1} = T_n - \frac{s(T_n, P) - s}{\partial s / \partial T)_P} \quad (29)$$

where $\partial s/\partial T)_P = C_P/T$ and C_P is evaluated by Eq. (17).

6. Application of the procedures

The foregoing procedures are utilized to develop computer programs which calculate thermodynamic properties for CO₂, HFC-134a and HCFC-22 with two independent properties given. The outputs of the program are compared with those of NIST Webbook⁽⁶⁾ confirming the correctness. Then found is the relation between temperature and pressure at which constant-pressure specific heat becomes a maximum for supercritical CO₂.

CO₂ refrigeration system makes a supercritical cycle. Thus gas coolers where supercritical heat transfer process occurs are under investigation. As a result of an experimental study on the heat transfer characteristics of gas cooler, Olson⁽¹⁴⁾ reported that the heat transfer coefficient enhances when temperature approaches T_m at which constant-pressure specific heat has a maximum. Therefore, it is essential to figure out the values of T_m at a given pressure. Figure 3 shows the constant-pressure specific heat as a function of temperature at several pressures. It is noted there is a maximum

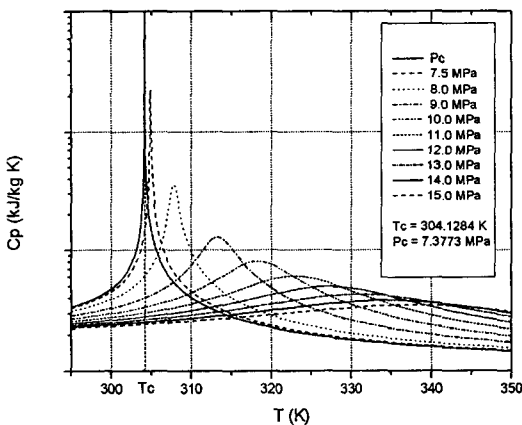


Fig. 3 Isobaric heat capacity versus temperature diagram for CO₂.

which increases as pressure decreases approaching the critical point where the specific heat becomes infinity. As pressure increases, the maximum specific heat decreases. Maximum point, however, is hardly observed beyond 14 MPa. Figure 4 shows the relation between T_m and pressure. Slight curvature is observed so that the curve is fitted to a quadratic equation,

$$y = ax + bx^2 \quad (30)$$

where $x = P_r - 1$, $y = T_r - 1$, $P_r = P/P_c$ and $T_r = T/T_c$. Fitting result yields $a = 0.14282$, $b = -0.035465$ with a maximum deviation of 0.25%. Equation (30) is valid when $P_c \leq P \leq 14$ MPa and $T_c \leq T \leq 335$ K.

7. Conclusions

Calculation procedures of thermodynamic properties are discussed. For thermodynamic consistency and computer time reduction and to check the application range appropriately, auxiliary equations are developed, as necessary. With a given set of two independent properties, standard procedures to find out the phase and then, by adjusting specific volume or tem-

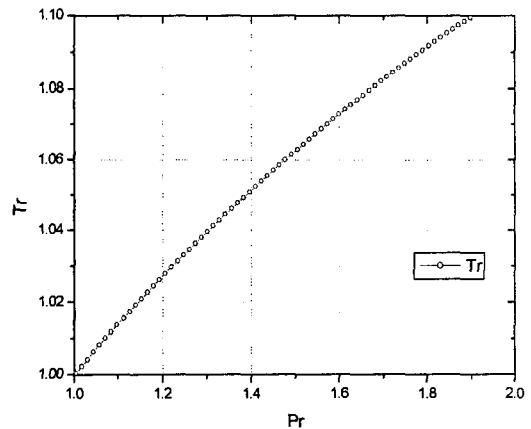


Fig. 4 $P_r - T_r$ diagram for CO₂.

perature, to calculate other unknown properties are suggested. The procedures are used to develop computer programs which calculate thermodynamic properties for carbon dioxide, HFC-134a, and HCFC-22. The programs are applied to find a correlation between temperature and pressure at which constant-pressure specific heat for supercritical carbon dioxide has a maximum.

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References

1. <http://www.winsim.com/steam/steam.html>
2. <http://www.propath.mech.kyushu-u.ac.jp/>
3. <http://www.uidaho.edu/~cats/>
4. McLinden, M. O., Klein, S. A., Lemmon, E. W. and Peskin, A. P., 1998, NIST Thermodynamic and transport properties of refrigerants and refrigerant mixtures database (REFPROP), version 6.0, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.
5. <http://www.chemicalogic.com/>
6. <http://webbook.nist.gov/chemistry/fluid/>
7. Span, R. and Wagner, W., 1996, A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, Vol. 25, No. 6, pp. 1509-1596.
8. Tillner-Roth, R. and Baehr, H. D., 1994, An international standard formulation for the thermodynamic properties of 1,1,1,2-tetrafluoroethane (HFC-134a) for temperatures from 170 K to 455 K and pressures up to 70 MPa, *J. Phys. Chem. Ref. Data*, Vol. 23, No. 5, pp. 657-729.
9. Kamei, A., Beyerlein, S. W. and Jacobsen, R. T., 1995, Application of nonlinear regression in the development of a wide range formulation for HCFC-22, *International Journal of Thermophysics*, Vol. 16, No. 5, pp. 1155-1164.
10. Moran, M. J. and Shapiro, H. N., 1993, *Fundamentals of Engineering Thermodynamics*, SI ed., John Wiley and Sons, New York, p. 472.
11. Wagner, W., Mark, V. and Pruß, A., 1993, A new equation of state for chlorodifluoromethane (R22) covering the entire fluid region from 116 K to 550 K at pressures up to 200 MPa, *Int. J. Refrig.*, Vol. 16, No. 6, pp. 373-389.
12. Park, K. K., 2001, A preliminary study on the form of vapor pressure equation for refrigerants, *Proceedings of the SAREK 2001 Winter Annual Conference*, pp. 133-137.
13. Park, K. K., 1998, A new type of saturated vapor density correlation for refrigerants, *Korean Journal of Air-Conditioning and Refrigeration Engineering*, Vol. 10, No. 5, pp. 550-557.
14. Olson, D. A., 2000, Heat transfer of supercritical carbon dioxide flowing in a cooled horizontal tube, IIF-IIR Commission B1, BE, E1, and E2, Purdue University, USA, pp. 251-258.