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ISOBARIC HEAT CAPACITY OF METHANE
OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE

BY

Edward W. Sladjeski

Submitted in Partial Fulfillment
of the Requirements
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With the extension of operating variables of chemical processes into high ranges of temperatures and pressures, lack of adequate design data has hampered reliable design of equipment and prediction of results, forcing attention to be focused on more accurate sources of thermodynamic properties. Much excellent experimental data are now available for the properties of pure compounds and mixtures in the ranges of temperatures and pressures readily controlled in the laboratory and pilot plant. Calculated values derived from the experimental data are accurate, and may be applied throughout the experimental ranges when the proper precautions and techniques are applied. Extrapolations beyond the ranges of experimental work must be done with caution and proper cognizance taken of the fact. Equations of state have been developed to permit interpolations and some occasional extrapolations. Here again, care must be exercised not to exceed the permissible ranges of variables specified for the particular equation of state employed. Generalized methods of calculating data are valuable and serve a distinct purpose when no other means are available. However, calculations of values of thermodynamic properties of substances outside ranges covered by available reliable data are best made from proper equations of state. In this manner, properties of matter may be obtained at elevated temperatures and pressures with some measure of assurance of accuracy.

Several recent equations of state include that of Beattie and Bridgeman (1), and that of Benedict, Webb and Rubin (2). The development of the Benedict-Webb-Rubin equation of state for the simpler paraffinic hydrocarbons offers an excellent tool for deriving thermodynamic properties of pure hydrocarbons at temperature-

Erp

pressure ranges above those for which experimental data are available. A recent attempt to apply an equation of state for calculation of data at elevated temperatures and pressures is that of Ellenwood, Kulik and Gay (3), who calculated the specific heats of several gases throughout the range of 400°R to 4500°R and 0 to 10,000 PSIA employing the Beattie-Bridgeman equation. The present paper presents a compilation of specific heats of methane calculated by application of thermodynamic relationships and the Benedict-Webb-Rubin equation of state.

Several recent studies of the isobaric specific heat of methane include those of Edmister (4), Budenholtzer, Sage and Lacey (5), and Ellenwood, Kulik and Gay cited previously. The values of isobaric heat capacity of methane reported by Edmister were computed from work based on the P-V-T data of Kvalves and Gaddy (6), and of Keyes and Burks (7), and atmospheric specific heats of methane of Eucken and Lude (8). The range covered included temperatures of -70°C to 200°C and pressures of 1 to 120 atmospheres. Since the isothermal change in the isobaric heat capacity with change in pressure is rather sensitive to minor uncertainties in P-V-T data when based upon them, Edmister's results are not in satisfactory agreement with those obtained from Joule-Thomson data. Specific heats calculated from Joule-Thomson coefficients are less subject to error than those calculated from P-V-T data.

Budenholtzer, Sage and Lacey evaluated isobaric heat capacities for methane from experimental Joule-Thomson coefficients. They report an uncertainty of not more than one percent in their computed values of heat capacity, except where the heat capacities are subject to possible later modifications of the spectroscopic value of the heat capacity at infinite dilution. Although Buden-

holtzer, et al, attribute the differences between their own values and those reported by Edmister to the discrepancies between the two sets of atmospheric heat capacity values, Edmister's heat capacity of methane relative to an ideal gas, $C_p - C_{p^*}$, also shows considerable deviation, as may be seen by inspection of Fig. 2.

Ellenwood, Kulik and Gay applied the Beattie-Bridgeman equation considerably beyond the original range of application specified for the equation. Further discussion of the comparative accuracy of their work is included with the discussion of the author's results.

The Benedict-Webb-Rubin equation of state may be regarded as a modification of the Beattie-Bridgeman equation to enable a more accurate representation of the properties of fluids at high densities. The Beattie-Bridgeman equation does not correspond accurately with the P-V-T properties of gases above their critical density, whereas the equation of Benedict-Webb and Rubin fits data well for all four hydrocarbons - methane, ethane, propane and butane - up to about 1.8 times the critical density; but above this density, calculated pressures are high. Benedict, Webb and Rubin note that their equation reproduces observed P-V-T properties of the gas phase in the critical region; a property the Beattie-Bridgeman equation does not possess. Except for methane, calculated and observed critical temperature and pressure agree within 0.25°C and 0.4 atmospheres respectively. For methane, the agreement is 0.3°C and 1.5 atmospheres.

Because of this superiority, the Benedict equation should reproduce more accurately values of heat capacity of a real gas relative to heat capacity of gas exhibiting ideal behavior, $C_p - C_{p^*}$, than the Beattie-Bridgeman equation.

METHOD OF CALCULATION

Reference to any text on thermodynamics will establish that:

$$(1) \quad C_p - C_p^* = C_p - C_v^\infty - R$$

By adding and subtracting C_v on one side and rearranging, we get:

$$(2) \quad C_p - C_p^* = (C_p - C_v) + (C_v - C_v^\infty) - R$$

The Benedict-Webb-Rubin equation of state is given by Hougen and Watson (9) as:

$$(3) \quad P = RTd + (B_0RT - A_0 - \frac{C_0}{T^2})d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{Cd^3}{T^2}(1 + \gamma d^2)e^{-\gamma d^2}$$

Relationships for $(C_p - C_v)$ and $(C_v - C_v^\infty)$ in terms of the Benedict-Webb-Rubin equation of state may be developed from the following thermodynamic relationships:

$$(4) \quad \left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

$$(5) \quad C_p - C_v = -T \left(\frac{\partial P}{\partial T}\right)_V^2 / \left(\frac{\partial P}{\partial V}\right)_T$$

$$(6) \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{V} \left[R + \frac{B_0R}{V} + \frac{2C_0}{T^3V} + \frac{bR}{V^2} - \frac{2C}{V^2T^3} (1 + \gamma/V^2) e^{-\gamma/V^2} \right]$$

$$(7) \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{6}{T^4V^2} \left[-C_0 + \frac{C}{V} (1 + \gamma/V^2) e^{-\gamma/V^2} \right]$$

$$(8) \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V} \left[\frac{RT}{V} + \frac{2}{V^2} (B_0RT - A_0 - \frac{C_0}{T^2}) + \frac{3}{V^3} (bRT - a) + \frac{6a\alpha}{V^6} + \frac{C e^{-\gamma/V^2}}{V^3 T^2} \left(3 + \frac{3\gamma}{V^2} - 2 \left(\frac{\gamma}{V^2}\right)^2 \right) \right]$$

Substituting in equation (4) and (5) and performing the indicated mathematical manipulations, we get:

$$(9) \quad C_v - C_v^\infty = \frac{6C_0}{T^3V} + \frac{6C}{T^3V} (e^{-\gamma/V^2} - 1) + \frac{3C e^{-\gamma/V^2}}{T^3V^2}$$

$$(10) \quad C_p - C_v = \frac{T \left[R + \frac{B_0R}{V} + \frac{2C_0}{T^3V} + \frac{bR}{V^2} - \frac{2C}{V^2T^3} (1 + \gamma/V^2) e^{-\gamma/V^2} \right]^2}{V \left[\frac{RT}{V} + \frac{2}{V^2} (B_0RT - A_0 - \frac{C_0}{T^2}) + \frac{3}{V^3} (bRT - a) + \frac{6a\alpha}{V^6} + \frac{C e^{-\gamma/V^2}}{V^3 T^2} \left(3 + \frac{3\gamma}{V^2} - 2 \left(\frac{\gamma}{V^2}\right)^2 \right) \right]}$$

Since equations (3), (9) and (10) are implicit in temperature, T , and specific volume, V , they are solved easiest by assuming a series of values of Volume, V , for a particular temperature, T . The solutions of equations (9) and (10), $(C_v - C_v^\infty)$ and $(C_p - C_v)$ respectively, are then substituted in equation (2), and $(C_p - C_p^*)$ calculated. A plot of $C_p - C_p^*$ versus pressures for a specific temperature was made and interpolated values of $C_p - C_p^*$ for pressures of 500, 1000, 1500 and 2000 to 10,000 PSIA in steps of 1000 PSIA picked off. Temperatures selected for purposes of calculation were 300, 350, 400, 500, 600, 800 and 1000°K. Five place logarithms were used throughout the calculations. A final plot of $(C_p - C_p^*)$ versus temperature with pressure as parameters was then made and is shown in Figure 1.

Since spectroscopic values of heat capacity at infinite dilution are subject to constant modification, values of $C_p - C_p^*$, heat capacity of methane relative to that of an ideal gas, are presented. For purposes of application to a specific problem involving heat capacity of methane, values at infinite dilution, C_p^* , at the required temperature should be added to values of $C_p - C_p^*$ presented in this paper. The API Tables (10) may be consulted for values of C_p^* .

DISCUSSION OF RESULTS

Since the value of C_p^* , heat capacity of methane at infinite dilution is subject to constant revision, a discussion of the merits of various investigations of methane heat capacity data should be limited to the values of $C_p - C_p^*$, heat capacity of methane relative to that of a gas exhibiting ideal behavior. Edmister's results were presented by him in tabular form for pressures of 1 to 120 atmospheres. Since heat capacity at one atmosphere is virtually the same as heat capacity at infinite dilution, values of $C_p - C_p^*$ may be calculated by subtracting C_p at one atmosphere from C_p at any other pressure. A cross-plot of the tabulated values gave interpolated results at 500, 1000, 1500 PSIA for a series of temperatures.

Budenholtzer, et al, present a tabulation of heat capacities for temperatures ranging from 70°F to 220°F and pressures of 0, 250, 500, 750, 1000, 1250, 1500 PSIA. Values of $C_p - C_p^*$ were calculated by subtracting C_p at 0 PSIA from C_p at 500, 1000 and 1500 PSIA for the six temperatures specified. Ellenwood, et al, presented their data in graphical form which is difficult to read accurately because of the wide range covered. Only curves for 0, 500 and 1000 PSIA are available within the range common to the first two sources quoted. Here again, $C_p - C_p^*$ was computed by subtracting values of C_p at 0 PSIA from values at 500 and 1000 PSIA. A plot of $C_p - C_p^*$ versus temperature with pressure parameters of 500, 1000, 1500 PSIA was developed for all three literature sources and for the work presented in this paper for comparative purposes. As was noted above, there are no data given by Ellenwood at 1500 PSIA.

Since data derived from Joule-Thomson coefficients are believed to be more accurate than those based on P-V-T work, the curves of $C_p - C_p^*$ obtained from Budenholtzer's tabulation were used as a basis

for evaluating the accuracy of the heat capacity data calculated in this paper. Inspection of the three plots for 500, 1000 and 1500 PSIA reveals quite clearly that Edmister's data, as stated in the opening discussion, deviate substantially from Budenholtzer's, indicating errors in calculation of $C_p - C_p^*$ as well as discrepancies in atmospheric heat capacity values. A comparison of the results derived from application of the Beattie-Bridgeman equation by Ellenwood, et al, and the Benedict-Webb-Rubin equation by the author indicate that for temperatures above 150°F, the Benedict equation reproduces values of $C_p - C_p^*$ more accurately than the Bridgeman equation does. Below 150°F, both equations show a deviation from Budenholtzer's figures that obviously places low temperatures data derived from either equation of state in the questionable category. At 500 PSIA, the author's values are virtually identical with those of Budenholtzer, both curves appearing to be superimposed whereas the values calculated by Ellenwood are approximately 6% low. In all cases, the author's data appears to be a few percent higher than those of Ellenwood, et al, a trend apparently followed by Budenholtzer's values. In general, the upper limits of Budenholtzer's data are more nearly approximated by the results of the application of the Benedict-Webb-Rubin equation of state. It may be concluded therefore, that the calculation of isobaric heat capacities of methane by means of the Benedict-Webb-Rubin equation of state gives more nearly accurate results than use of the Beattie-Bridgeman equation, as was expected.

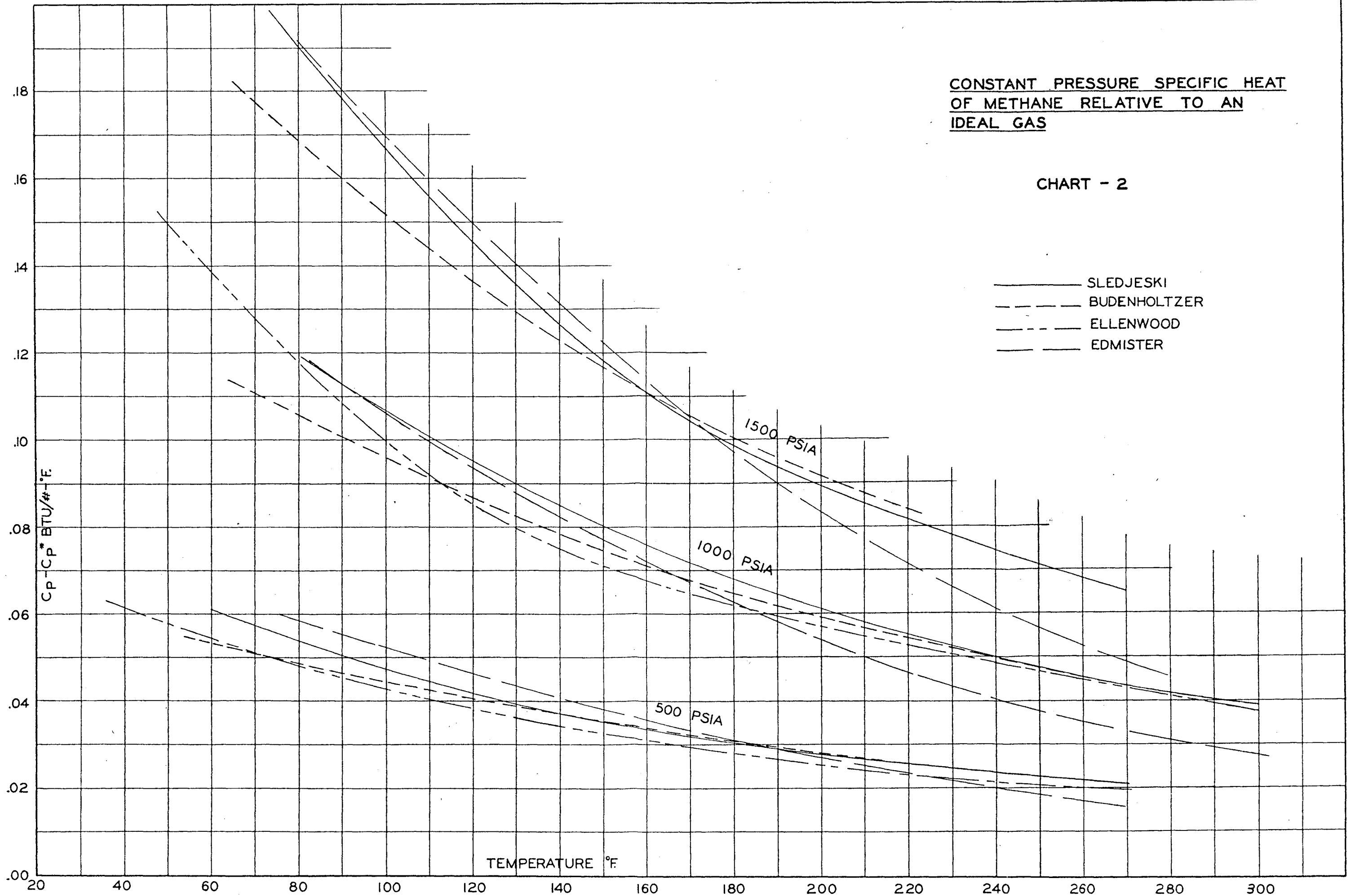
The author's values, based on the Benedict-Webb-Rubin equation of state, are recommended for application to specific problems involving heat capacity of methane above 220°F and 1500 PSIA. Below this range, the most accurate work is believed to be that of Budenholtzer, Sage and Lacey.

NOMENCLATURE

- C_p - Constant-pressure heat capacities, molal basis.
- c_p - Specific heat at constant pressure, BTU/#-°F; CAL/GM-°C.
- c_p* - Constant-pressure specific heat, gas exhibiting ideal behavior.
- C_v - Constant-volume heat capacities, molal basis.
- c_v - Constant-volume specific heat BTU/#-°F.
- c_v[∞] - Constant-volume specific heat at zero pressure or infinite volume.
- T - Temperature, degrees Kelvin.
- V̄ - Molal Volume, liters/gram - mol.
- d - Molal density, gram mols/liter.
- P - Pressure, atmospheres.
- R - Gas Constant = 0.08207 liter-atm/gram mol - °Kelvin.
- B₀, A₀, C₀, b, a, c - Benedict-Webb-Rubin Equation of State Constants
Y, ∞ (See sample calculation)
- C_p-C_p* - Heat capacity of a real gas relative to heat capacity of gas exhibiting ideal behavior.

CONSTANT PRESSURE SPECIFIC HEAT
OF METHANE RELATIVE TO AN
IDEAL GAS

CHART - 2



PART I - SAMPLE CALCULATION

$$P = RT/V + \frac{(B_0RT - A_0 - C_0)}{T^2} \frac{1}{V^2} + (bRT - a) \frac{1}{V^3} + a\alpha/V^6 + \frac{c(1 + \gamma/V^2)}{T^2 V^3} e^{-\gamma/V^2}$$

T = 1000°K
R = 0.08207

B₀ = 0.042600
A₀ = 1.85500
C₀ = 22570
b = 0.00338004

a = 0.049400
c = 2545
γ = 0.006000
α = 0.00124359

Units: Atmospheres, Liters, Gram-Moles, Degrees Kelvin

V	RT/V	$(B_0RT - A_0 - C_0/T^2) \frac{1}{V}$	$(bRT - a) \frac{1}{V^3}$	$a\alpha/V^6$	$\frac{ce^{-\gamma/V^2}(1 + \gamma/V^2)}{T^2 V^3}$	P-ATM	P-PSIA
.7	117.24	3.3032	.66452	-----	.0074189	121.22	1781.4
.6	136.78	4.4961	1.0552	-----	.011781	142.35	2092.0
.5	164.14	6.4744	1.8234	-----	.020355	172.45	2534.4
.45	182.38	7.9932	2.4956	-----	.027916	192.90	2834.9
.4	205.17	10.116	3.5614	-----	.039738	218.89	3216.9

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PART II - SAMPLE CALCULATION

$$C_V - C_V^\infty = \frac{6 C_0}{T^3 V} + \frac{6 c}{T^3} (e^{-Y/V^2} - 1) + \frac{3c e^{-Y/V^2}}{T^3 V^2}$$

T = 1000°K Same Units and Constants as Part I

V	$6 C_0/T^3 V$	$\frac{6c (e^{-Y/V^2} - 1)}{T^3}$	$\frac{3ce^{-Y/V^2}}{T^3 V^2}$	$C_V - C_V^\infty$ Liter-Atm/Gr Mol -°K
.7	.00019345	-.000030973	.000015392	.00017787
.6	.00022570	-.000042018	.000020858	.00020454
.5	.00027084	-.000060317	.000029816	.00024034
.45	.00030093	-.000074314	.000036603	.00026322
.4	.00033855	-.000093706	.000045962	.00029080

PART III - SAMPLE CALCULATION

$$C_p - C_v = T \frac{[R + B_0 R/V + 2 C_0/T^3 V + bR/V^2 - 2c/V^2 T^3 (1 + Y/V^2) e^{-Y/V^2}]^2}{V [RT/V + 2/V^2 (B_0 RT - A_0 - C_0/T^2) + 3/V^3 (bRT - a) + 6ac/V^6 + \frac{ce - Y/V^2}{V^3 T^2} (3 + \frac{3Y - 2Y^2}{V^2 \frac{Y^2}{V^4}})]}$$

T = 1000°K

Same Units and Constants as Part I

(1)	(2)	(3)	(4)	(5)	(6)	(7)
V	$B_0 R/V$	$2C_0/T^3 V$	bR/V^2	$\frac{-2ce}{V^2 T^3} (1 + Y/V^2) e^{-Y/V^2}$	$R + C_0(2+3+4+5)$	RT/V
.7	.0049944	.00006448	.00056611	-.000010386	.087684	117.24
.6	.0058269	.00007523	.00077055	-.000014137	.088729	136.78
.5	.0069924	.00009028	.0011096	-.000020354	.0902412	164.14
.45	.0077692	.00010031	.0013699	-.000025125	.091284	182.38
.4	.0087404	.00011285	.0017337	-.000031790	.092625	205.17

PART III - SAMPLE CALCULATION

(Continued)

	(8)	(9)	(10)	(11)	(12)	(13)
V	$2/V^2 (E_0 hT - A_0 - C_0/T^2)$	$3/V^2 (b hT - a)$	$\frac{ce^{-Y/V^2}}{V^3 T^2}$	$(3+3Y - \frac{2Y^2}{V^4})$	$6 a^2/V^6$	Col (7+8+10+11+12) Cp-Cv Liter Atmos/Lr Mol-°K $\frac{T [Col. 8]^2}{V [Col. 13]}$
.7	6.6004	1.99356	.0223	---	125.862	.087267
.6	8.9922	3.1656	.0353	---	148.98	.088076
.5	12.0488	5.4702	.061043	---	182.62	.089186
.45	15.9864	7.4868	.081116	---	205.934	.089923
.4	20.232	10.6812	.11911	.009	236.21	.090798

PART IV - SAMPLE CALCULATION

$$C_p - C_p^* = (C_p - C_v) + (C_v - C_v^{\infty}) - R$$

$$T = 1000^{\circ}K$$

$$\text{Conversion Factor } \frac{\text{Liter-Atm}}{\text{GM Mol-}^{\circ}K} \text{ to } \frac{\text{Cal/GR- K}}{\text{GM Mol-}^{\circ}K} = \frac{24.218}{16.04} = 1.5098$$

V Liters <u>GM-Mol</u>	P-ATM	P-PSIA	$C_p - C_v$ <u>Liter-Atm</u> <u>GM Mol-}^{\circ}K</u>	$C_v - C_v^{\infty}$ <u>Liter-Atm</u> <u>GM Mol-}^{\circ}K</u>	$C_p - C_p^*$ <u>Liter-Atm</u> <u>GM-Mol-}^{\circ}K</u>	$C_p - C_p^*$ <u>CAL/GR-}^{\circ}K</u>
.7	121.22	1781.4	.087267	.00017787	.005375	.0081154
.6	142.35	2092.0	.098076	.0020454	.006211	.0093776
.5	172.45	2534.4	.089186	.00024034	.007356	.011106
.5	192.90	2834.9	.089923	.00026322	.008116	.012251
.4	217.69	3216.9	.090798	.00029050	.009020	.013618

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