Thermodynamic Properties of Cyclopropane

DAVID C.-K. LIN[1] and JOHN J. McKETTA
The University of Texas at Austin, Austin, Tex. 78712

I. HAROLD SILBERBERG[2]
Texas Petroleum Research Committee, Austin, Tex. 78712

The enthalpy and entropy of cyclopropane were numerically calculated from experimental pressure-volume residual-temperature data. In conjunction with ideal state thermodynamic properties from the literature, the Mollier diagram of cyclopropane was constructed for the temperature range of 525–855°R and a pressure up to 4500 psia.

The basic equations employed for the evaluation of thermodynamic properties from the volume residual data were the same used by Hsu and McKetta (*1*). Equations 1–6 are the fundamental relationships for the enthalpy and entropy.

$$\Delta H_{P,T} = \Delta H_T{}^\circ + H_P + (\Delta H_v)_{T_0} \tag{1}$$

$$\Delta S_{P,T} = \Delta S_T{}^\circ + S_P + (\Delta S_v)_{T_0} \tag{2}$$

$$\Delta H_T{}^\circ = \int_{T_0}^{T} C_P{}^\circ \, dT \tag{3}$$

$$\Delta S_T{}^\circ = \int_{T_0}^{T} \frac{C_P{}^\circ}{T} \, dT \tag{4}$$

$$H_P = J\left[\int_0^P \left[T\left(\frac{\partial\gamma}{\partial T}\right)_P - \gamma\right]_T dP - \int_0^{P_0} \left[T\left(\frac{\partial\gamma}{\partial T}\right)_P - \gamma\right]_{T_0} dP\right] \tag{5}$$

$$S_P = J\int_0^P \left[\left(\frac{\partial\gamma}{\partial T}\right)_P\right]_T dP - R\ln(P/P_0) - J\int_0^{P_0} \left[\left(\frac{\partial\gamma}{\partial T}\right)_P\right]_{T_0} dP \tag{6}$$

The experimental volume residual data (*5*) were smoothed and interpolated into a pressure-volume residual-temperature array by means of the least-squares method described by Lin et al. (*5*). A localized equation of state

$$\gamma = C_1 + C_2P + C_3P^2 + C_4T + C_5PT + C_6P^2T + C_7T^2 + C_8PT^2 + C_9P^2T^2 \tag{7}$$

was used analytically to evaluate the entire pressure integrals in Equations 5 and 6 by integration over subintervals with 5 psia increments. The details were given by Lin (*4*).

The fugacity coefficient at each new increment of pressure was calculated by the following equation:

$$\nu_2 = \nu_1 \exp\left[\frac{-1}{RT}\int_{P_1}^{P_2} \gamma \, dP\right] \tag{8}$$

Specific volumes were also evaluated from the volume residuals using the relationship

$$V = \frac{RT}{P} - \gamma(T,P) \tag{9}$$

REFERENCE STATE

The saturated liquid state of cyclopropane at 525°R was used as the reference state of the present work. Here the vapor pressure is 87.787 psia in accordance with the Nernst equation of Lin et al. (*5*).

SOURCES OF DATA

The volume residuals used in evaluating the enthalpy and entropy were interpolated from the data of Lin et al. (*5*). The heats and entropies of vaporization, the orthobaric densities, and the vapor pressures were calculated from the correlations of Lin et al. (*5*).

For the temperature range of the present work, the following relationship was fitted by the least-squares method to the ideal state heat capacity data of Kistiakowsky et al. (*2, 3*):

$$C_P{}^\circ = 2.520225 + 9.055728(10^{-3})T + 2.968219(10^{-5})T^2 - 1.650506(10^{-8})T^3 \tag{10}$$

where T is the absolute temperature, °R. The standard error of the regression was 0.006 Btu/lb °F, and the average absolute deviation of the heat capacity data from those calculated by Equation 10 was 0.144%. Subsequently, the ideal state enthalpy and entropy changes were calculated from Equations 3 and 4 by means of Equation 10. The agreement between the calculated entropies and values in the literature (*3*) was good, with a maximum deviation of 0.00025 Btu/lb °R and a standard deviation less than 0.0001 Btu/lb °R.

THERMODYNAMIC PROPERTIES AND MOLLIER DIAGRAM

Enthalpies and entropies, specific volumes, and the fugacity coefficients of cyclopropane in the vapor phase are listed in Table I (complete table deposited with the ACS Microfilm Depository Service).

The saturated vapor state thermodynamic properties were evaluated by integrating to the vapor pressure for each isotherm. The results were graphically smoothed. The enthalpies and entropies for the saturated liquid were obtained by subtracting the heats and entropies of vaporization, respectively, from the smoothed values. The thermodynamic properties of the saturated states of cyclopropane are summarized in Table II.

The enthalpy and entropy of cyclopropane in the two-phase region were obtained from the following two equations:

$$H_x = H_g - (1 - x)\Delta H_v \tag{11}$$

$$S_x = S_g - (1 - x)\Delta S_v \tag{12}$$

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[1] Present address, E. I. du Pont de Nemours & Co., Old Hickory, Tenn.

[2] To whom correspondence should be addressed.

Table I. Thermodynamic Functions of Gaseous Cyclopropane

Reference State: $H = 0$ and $S = 0$ for saturated liquid at 525°R and 87.787 psia

T = Temperature, °R
P = Pressure, psia
V = Volume, ft³/lb
H = Enthalpy, Btu/lb
S = Entropy, Btu/lb, °R
ν = Fugacity coefficient, f/P

T	P	V	H	S	ν
525	5	26.63	185.7	0.4845	0.9947
	10	13.24	185.4	0.4514	0.9893
	15	8.781	185.0	0.4318	0.9840
	20	6.548	184.7	0.4179	0.9787
	25	5.208	184.3	0.4069	0.9733
	30	4.314	184.0	0.3979	0.9680
	40	3.195	183.2	0.3833	0.9572
	50	2.522	182.3	0.3717	0.9463
	60	2.071	181.4	0.3618	0.9352
	70	1.748	180.3	0.3530	0.9239
	80	1.503	179.0	0.3450	0.9124
855	5	43.55	322.6	0.6828	0.9988
	20	10.85	322.1	0.6169	0.9951
	60	3.580	320.6	0.5637	0.9853
	100	2.126	319.1	0.5383	0.9755
	140	1.503	317.6	0.5211	0.9658
	200	1.035	315.4	0.5024	0.9514
	300	0.6715	311.8	0.4802	0.9276
	400	0.4893	308.1	0.4635	0.9043
	500	0.3798	304.2	0.4497	0.8813
	600	0.3068	300.2	0.4376	0.8588
	800	0.2151	291.4	0.4162	0.8150
	1000	0.1598	280.4	0.3953	0.7728
	1200	0.1219	268.6	0.3754	0.7322
	1500	0.08628	258.2	0.3566	0.6743
	2000	0.05756	233.8	0.3206	0.5931
	2500	0.04697	220.2	0.2991	0.5339
	3000	0.04210	213.4	0.2863	0.4925
	3500	0.03919	209.3	0.2771	0.4633
	4000	0.03725	206.8	0.2700	0.4425
	4500	0.03581	205.1	0.2641	0.4276

The resulting data of the above calculations were used to plot the Mollier diagram (Figure 1) giving the enthalpy and entropy isotherms, the isobars, the saturation curve, and the quality lines for temperatures from 525–855°R and for pressures from 5–4500 psia.

DISCUSSION

The internal consistency of the Mollier diagram was estimated by the relationship

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{13}$$

The slope at a point on an isobar in the enthalpy-entropy diagram should equal the temperature at that point. Integrating Equation 13 at constant pressure gives

$$\left[H_2 - H_1 = T_2S_2 - T_1S_1 - \int_{T_1}^{T_2} S\,dT\right]_P \tag{14}$$

The isobaric enthalpy changes, from T_1 to T_2, at six different pressures (60, 600, 1000, 2000, 3000, and 4000 psia) were calculated by means of Equation 14 from the entropy data of Table I over temperature intervals ranging from 330–130°R. The integration required in Equation 14 was performed numerically by means of Simpson's rule. The isobaric enthalpy changes thus calculated are presented in Table III, from which it can be seen that deviations from the data of Table I do not exceed 0.1 Btu/lb.

In light of the very high internal consistency of the calculated results and accuracy of the measured PVT data, the reliability of the enthalpy data is believed to be within ±0.8 Btu/lb and of the entropy data, ±0.0005 Btu/lb °R.

Table III. Internal Consistency Check for Evaluation of Thermodynamic Functions

Temp range, °R	Pressure, psia	ΔH(Btu/lb) Equation 14	ΔH(Btu/lb) Table I
525–855	60	139.3	139.2
685–855	600	106.4	106.4
725–855	1000	144.7	144.6
725–855	2000	112.1	112.0
725–855	3000	94.6	94.7
725–855	4000	88.9	88.9

Table II. Thermodynamic Properties of Saturated Cyclopropane

Temp, °R	Pressure, psia	Vol, ft³/lb Liquid	Vol, ft³/lb Vapor	Enthalpy, Btu/lb Liquid	Enthalpy, Btu/lb ΔH_v	Enthalpy, Btu/lb Vapor	Entropy, Btu/lb °R Liquid	Entropy, Btu/lb °R ΔS_v	Entropy, Btu/lb °R Vapor	Fugacity Coeff, f/P
525	87.79	0.02552	1.248	0.0	177.9	177.9	0.0000	0.3389	0.3389	0.9032
535	102.46	0.02585	1.120	5.2	174.3	179.5	0.0092	0.3258	0.3350	0.8925
545	118.85	0.02619	0.9960	10.6	170.5	181.1	0.0194	0.3129	0.3323	0.8818
555	137.06	0.02656	0.8796	16.1	166.7	182.8	0.0294	0.3003	0.3297	0.8709
565	157.22	0.02696	0.7736	21.9	162.6	184.5	0.0394	0.2879	0.3273	0.8595
575	179.45	0.02739	0.6788	27.7	158.5	186.2	0.0495	0.2756	0.3251	0.8480
585	203.88	0.02785	0.5952	33.7	154.1	187.8	0.0600	0.2634	0.3234	0.8361
595	230.63	0.02836	0.5219	40.0	149.5	189.5	0.0702	0.2513	0.3215	0.8241
605	259.86	0.02890	0.4579	46.5	144.7	191.2	0.0805	0.2392	0.3197	0.8117
615	291.70	0.02951	0.4021	53.0	139.6	192.6	0.0909	0.2271	0.3180	0.7991
625	326.32	0.03017	0.3533	59.6	134.2	193.8	0.1012	0.2148	0.3160	0.7864
635	363.88	0.03091	0.3106	66.1	128.5	194.6	0.1113	0.2023	0.3136	0.7733
645	404.57	0.03173	0.2729	73.0	122.2	195.2	0.1214	0.1895	0.3109	0.7601
655	448.56	0.03268	0.2396	80.1	115.4	195.5	0.1321	0.1762	0.3083	0.7469
665	496.07	0.03378	0.2099	87.4	107.9	195.3	0.1427	0.1623	0.3050	0.7334
675	547.32	0.03508	0.1830	95.4	99.39	194.8	0.1542	0.1472	0.3014	0.7198
685	602.53	0.03669	0.1584	103.9	89.48	193.4	0.1663	0.1306	0.2969	0.7061
695	661.98	0.03882	0.1351	113.9	77.39	191.3	0.1802	0.1113	0.2915	0.6918
705	725.94	0.04199	0.1118	126.1	61.08	187.2	0.1969	0.0866	0.2835	0.6769
715	794.70	0.04954	0.08214	151.0	29.94	180.9	0.2309	0.0419	0.2728	0.6616

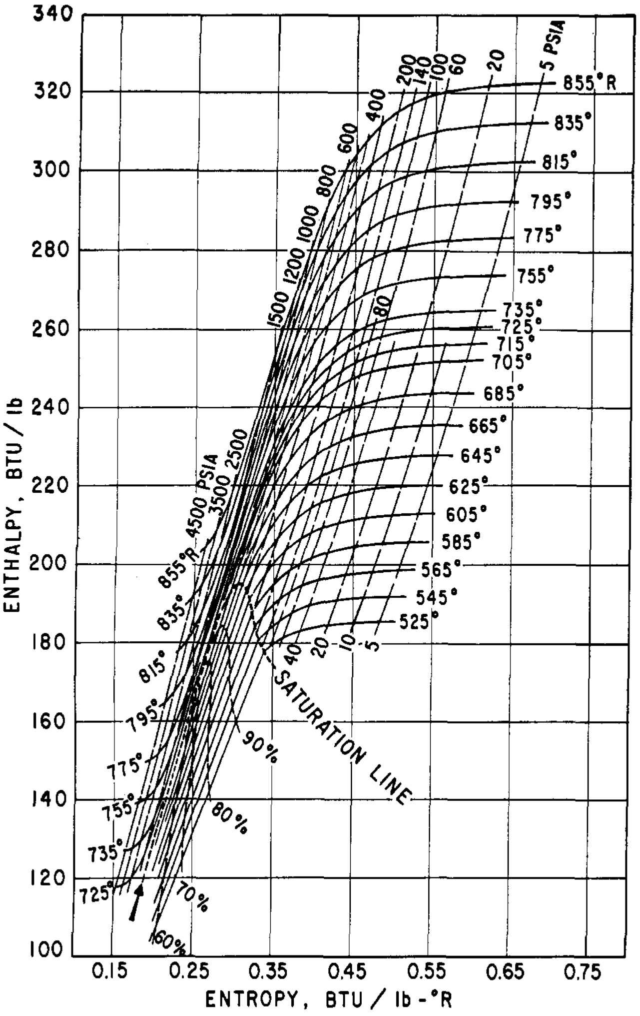

Figure 1. Mollier diagram of cyclopropane in vapor phase

NOMENCLATURE

$C_P°$ = Heat capacity at constant pressure in ideal gas state, Btu/lb °R
f = Fugacity
H_g = Enthalpy of saturated vapor, Btu/lb
$\Delta H_{P,T}$ = Enthalpy at P,T above the saturated liquid state at P_0,T_0, Btu/lb
$\Delta H_T°$ = Change of ideal state enthalpy from T_0 to T, Btu/lb
$(\Delta H_v)_{T_0}$ = Heat of vaporization at the reference temperature T_0, 177.924 Btu/lb
H_x = Enthalpy of the vapor-liquid mixture, Btu/lb
J = Dimensional constant for cyclopropane, 0.004400354 (Btu/lb)(ft^3/lb-mol)$^{-1}$ (psia)$^{-1}$
P = Pressure, psia
P_0 = Reference pressure, 87.787 psia
R = Cyclopropane gas constant, 0.25502 (psi) (ft^3)/(°R) (lb), 0.047222 (Btu)/(°R) (lb)
S_g = Entropy of the saturated vapor, Btu/lb °R
$\Delta S_{P,T}$ = Entropy at P,T above the saturated liquid state at P_0,T_0, Btu/lb °R
$\Delta S_T°$ = Change of ideal state entropy from T_0 to T, Btu/lb °R
$(\Delta S_v)_{T_0}$ = Entropy of vaporization at the reference temperature T_0, 0.3389 Btu/lb °R
S_x = Entropy of vapor-liquid mixture, Btu/lb °R
T = Temperature, °R
T_0 = Reference temperature, 525°R
V = Specific volume, ft^3/lb
x = Quality of the vapor-liquid mixture, lb vapor/lb of mixture
γ = Volume residual, $\frac{RT}{P} - V$, ft^3/lb
ν = Fugacity coefficient, f/P

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Estimation of Heats of Formation of Binary Oxides

KLAUS SCHWITZGEBEL,[1] PHILIP S. LOWELL,[1] and TERRY B. PARSONS[1]
Tracor, Inc., Austin, Tex. 78721

KARL J. SLADEK[2]
Department of Chemical Engineering, The University of Texas at Austin, Austin, Tex. 78712

Calculation of gas solid reaction equilibria requires a variety of thermodynamic data. When the available data on a solid compound are incomplete, well-known methods can be used to estimate absolute entropies or heat capacities (*18*). The remaining information needed is the standard enthalpy of formation from the elements at 298.15°K, $\Delta H_f°$. The present investigation reports a method for estimating $\Delta H_f°$ for compounds formed from two oxides, such as $CaSO_4$ (from CaO and SO_3) or $Na_2Al_2O_4$ (from Na_2O and Al_2O_3).

This problem of estimating $\Delta H_f°$ arose during a study of processes for removing sulfur oxides from flue gas, using dry

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[1] Present address, Radian Corp., Austin, Tex. 78758.
[2] To whom correspondence should be addressed.