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New Enthalpy Increment Flow Calorimeter and Measurements on a Mixture of 68% Methane and 32% Propane[1]

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A new flow calorimeter for measuring isobaric enthalphy increment and Joule–Thomson effect was built and tested during the period 1987–1993. The calorimeter has several features that reduce the heat leakage better than previous designs; this includes thermal shields cooled by propane, a heat sink, and superinsulation on all piping. The temperature and pressure range covered by the calorimeter is 133 to 343 K and 0.17 to 14 MPa. Measurements on a mixture of 68.32% methane and 31.68% propane are presented. The enthalpy increment measurements have an average standard uncertainty of 0.08 $\mathrm{kJ \cdot kg^{-1}}$, or 0.22% of the enthalpy increment.

KEY WORDS: calorimetry; database; enthalpy; flow calorimeter; Joule–Thomson coefficient; methane; propane.

1. INTRODUCTION

Exact knowledge of the effect of pressure and temperature on enthalpy is of vital importance in the design of plants for liquefaction of natural gas. Existing correlations given for calculation of the enthalpy are not accurate enough and more experimental enthalpy measurements are needed to improve these correlations. Although the investigations presented are numerous, the results are still scattered for many of the mixtures, and some mixtures have not been investigated at all. Mixtures of methane and propane were examined previously at the University of Michigan in the

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1960s [1–10], but the composition of these mixtures was not equal to the one reported in this paper.

The flow calorimeters used in this type of study are either of the boil-off type of the electrically heated type. In the boil-off calorimeter, the fluids of interest are cooled by heat exchange with a boiling reference medium, and the enthalpy changes are then calculated from the amount of evaporated reference medium. In the electrically heated calorimeter, the fluids are heated directly by an internal electric heater.

In the boil-off calorimeter it is necessary to measure the mass flow of both the test fluid and the reference fluid, thus reducing the total accuracy. An electrically heated calorimeter was therefore designed for this study. The calorimeter is based on the design of Pieper [11] and incorporates several new features to reduce heat leakage; this includes thermal shields cooled by propane, a heat sink, and superinsulation on all internal piping.

Measurements on pure methane, ethane, nitrogen, and binary mixtures with these components including propane have been accomplished. The temperature range covered by the calorimeter is from 133 to 343 K and and the pressure range is from 0.17 to 14 MPa. This paper describes the results of measurements of a mixture of 68.32 % methane and 31.68 % propane. The standard uncertainty of this composition, $u(z_i)$, is ±0.037 %.

2. THE FLOW CALORIMETER

According to the flow diagram shown in Fig. 1, the test gas is compressed in a two-stage oil-free membrane compressor (SERA MV3506 II K), from a suction pressure of 0.115 ± 0.015 to 17.8 ± 0.5 MPa outlet pressure. The compressor incorporates water-cooling of the test gas after the first and second stages. The cylinder heads and oil sump are also water-cooled. From the compressor the test gas is fed to the mass-flow metering section, where the pressure is kept constant by a dome pressure regulator. To maintain accurate pressure, the regulator, fitted with an extended dome volume, is kept in a temperature-controlled bath. To avoid vibration-induced errors in the measurements, the mass flow meters are mounted on heavy concrete blocks on rubber vibration dampers and connected to the circuit by flexible tubes.

After the gas has passed the mass flow meters, the pressure is reduced and kept constant at the desired test-section pressure, again by using a dome pressure regulator. The test gas is then cooled to a temperature from 1 to 10 K below the test-section temperature. In the first heat exchanger the inlet test gas is cooled by the outlet test gas, which is usually cold due to the Joule–Thomson (JT) effect in the calorimeter, and in the second heat exchanger the test gas is cooled by propane or water. The test gas then

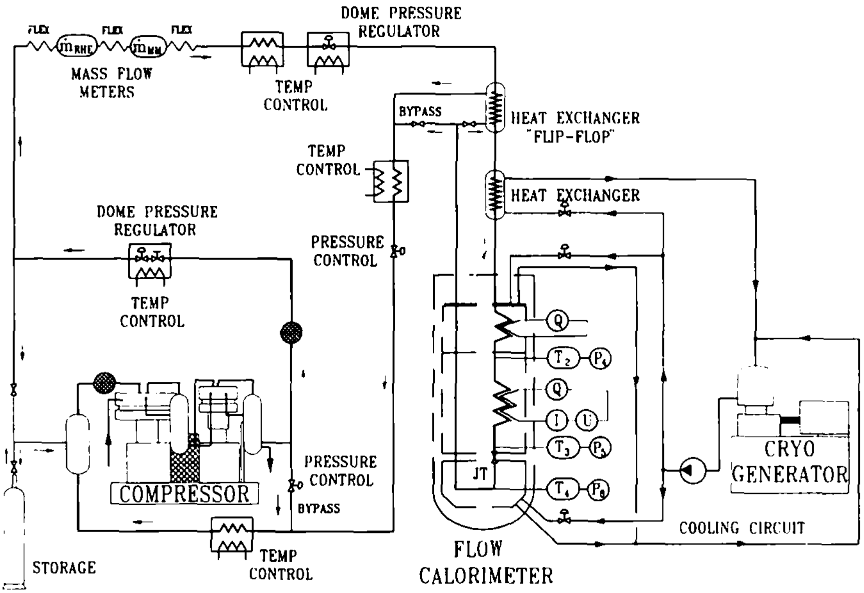

Fig. 1. Flow diagram of the calorimeter.

enters the calorimeter, where it is first heated to the desired temperature in the preheater. The preheater has a maximum power of 50 W and is controlled by a PID regulator (Lake Shore Cryotronics DRC 93C Temperature Controller) that keeps the test-gas temperature as close to the set point as possible, when the gas enters the test section.

In the test section, the gas is heated with constant electrical power through a 1.3-m Thermocoax heater element, mounted in the center of the flow tube, thus eliminating hot spots. The heater element has a 0.1-m cold end to reduce the conduction of heat out of the flow tube. The power supply system (HP 6633A DC) has a 100-W maximum electrical effect.

The temperature and pressure are measured before (T_2, P_4) and after (T_3, P_5) the heating section. From the heating section the gas passes through an adjustable JT valve, and the temperature and pressure are measured again (T_4, P_6). From the JT valve the gas passes through the heat exchanger, where it cools the inlet test gas.

The performance of the calorimeter is very sensitive to heat leakage from the surroundings. To reduce the heat leakage, the calorimeter is enclosed in a container evacuated to a pressure of $<10^{-2}$ Pa. A thermal sink is placed at the top of the vacuum container, and all inlet/outlet pipes to the calorimeter pass through this sink. The sink is divided into two sections; one is kept at the mean temperature of the isobaric section and is connected to the piping to this section. The other sink is kept at the JT valve outlet temperature and is connected to the piping from this section. Thus heat leakage to or from the surroundings along the piping should be eliminated.

Radiation shields are fitted around the heating section and JT section. In the low-temperature region, the shields and sink are cooled by a Philips cryogenerator (PPG 102S with hydrogen as working gas), using liquid propane as coolant. At higher temperatures, water baths (Haake N2) are used for cooling and heating. This allows the temperature of the shields to be adjusted independently of the operation of the calorimeter and kept at the average temperature of the test gas. Sixty layers of superinsulation (Alu Mylar 13 NRC-2) were used on the piping carrying the test gas. Figure 2 shows the vacuum container with insulated test section, thermal sink, and radiation shields.

The water baths cover the temperature range from 283.0 to 335.0 K, and the cryogenerator covers the range from 133.0 to 253.0 K. The inter-

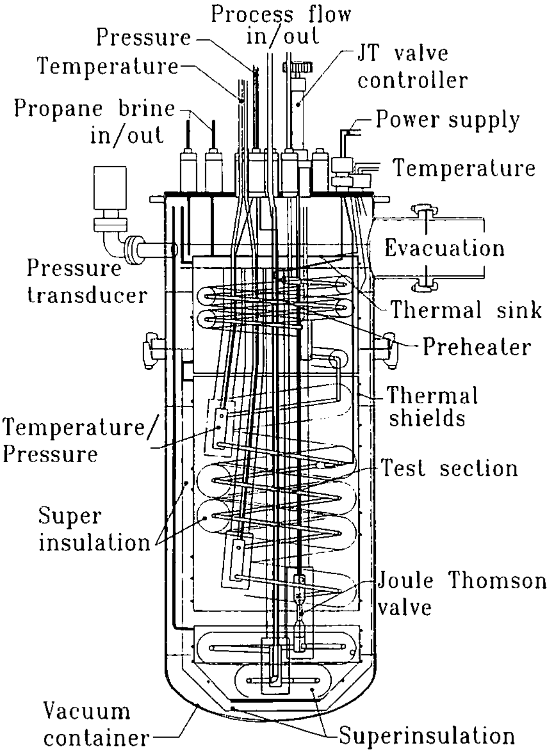

Fig. 2. Test section with radiation shields.

mediate temperature region could not be used as a starting condition in the calorimeter. It is still possible to get measurements that cover this region, either by heating the gas from the upper cold limit (253.0 K) or by isenthalpic throttling from the warm region.

The mass flow, $\dot{m}_{\mathrm{RHE}}$ and $\dot{m}_{\mathrm{MM}}$, is measured by two independent coriolis meters in series (Rheonik RHE 02 and Micro Motion DS 006S). Coriolis (vibrating U-tube) meters were chosen because they measure the mass flow directly due to the second law of Newton, i.e., not like the volumetric flow meters that need a density measurement or PVT equation to get the mass flow. The flow meters chosen are of different types, so as to detect possible nonrandom errors. The totalizer (integration) function of the meters is used together with stopwatches to get the average mass flow through the whole system. The flow meters are calibrated every fourth month.

The inlet pressure, P_4, is measured by a quartz pressure transducer (Digiquartz 1003 K). The pressure drop, P_4–P_5, in the heating section is given by a differential pressure transmitter (Honeywell STD120-E1H-00000-MB-P0D2), and the pressure after the JT valve, P_6, is measured by a quartz pressure transducer (Digiquartz 1002 K). The pressure cells are calibrated once a year.

The temperatures, T_2, T_3, and T_4, are determined by a resistance bridge (Automatic Systems Laboratories F26) and platinum resistance thermometers of type PT100 (Leeds & Northrup 0106025). The thermometers are calibrated once a year and are checked every fourth month with a reference thermometer that is traceable to international standards. The voltage, U, and current, I, are measured by Fluke 8840A meters, calibrated once a year.

All data, except the mass flow, are recorded directly on a PC as raw data. These raw data are transferred to a database and converted into SI units and corrected with calibration factors. The measured enthalpy can then be compared with equations of state (Soave–Redlich–Kwong, Peng–Robinson, LNGONE [12], and a new corresponding-states equation [13]). The database consists of 950 measurements from this calorimeter and 2500 data points from the open literature.

3. RESULTS AND DISCUSSION

3.1. Accuracy of the Measurements

The accuracy of the measurements of enthalpy increment, Δh, and integral JT coefficient, μ, is affected by the heat leakage and the accuracy of the instrumentation. These sources of uncertainty are evaluated in detail. A consistency check is performed to confirm the estimated uncertainty.

The uncertainty analysis is done in accordance with the guidelines given by the National Institute of Standards and Technology (NIST) [14]. All uncertainties are treated as so-called "Type B," where the standard uncertainty is estimated by means other than statistical methods on a large population. The term standard uncertainty, $u(x_i)$, is used for each component of uncertainty that contributes to the uncertainty of a measurement result by an estimated standard deviation.

Extensive experimental test runs and theoretical evaluations have been performed to find the heat leakage by radiation, conduction into the calorimeter, and conduction along the internal flow tubes. To get comparable numbers, all calculations have been performed at the worst case, i.e., conditions of maximum heat transfer. The condition of maximum heat transfer is then considered to be at the level of ±3 standard deviations.

The uncertainty cannot be given as a fixed value for all the test runs, because the measured enthalpy increment and JT effect are a function of several parameters of varying importance in different temperature and pressure regions. The standard uncertainties in the individual measurements are given in Table I. The uncertainties are for the final instrumentation of the calorimeter. The individual uncertainties, $u(x_i)$, are combined according to Eq. (1), giving the standard uncertainty of the enthalpy increment measurements, $u(\Delta h)$.

$$u(\Delta h)=\left[\sum_{i=1}^{N}\left(\frac{\partial \Delta h}{\partial x_i}\cdot u(x_i)\right)^2\right]^{0.5} \tag{1}$$

Table I. Standard Uncertainties in the Individual Measurements

Unit	Standard uncertainty, $u(x_i)$
$u(T_2)$, $u(T_3)$, $u(T_4)$	± 0.013 K
$u(P_4)$	± 0.0016 MPa
$u(P_5)$	$\pm 0.0016 + 8.5 \times 10^{-6}$ MPa
$u(P_6)$	± 0.0011 MPa
$u(I)$	± 0.0167% of reading $+ 13.3 \times 10^{-6}$ A, $I < 1.0$ A
	± 0.033% of reading $+ 13.3 \times 10^{-6}$ A, $I > 1.0$ A
$u(U)$	± 0.002% of reading $+/- 1.0$ V
$u(\dot{m}_{\mathrm{MM}})$	± 0.11% of reading
$u(\dot{m}_{\mathrm{RHE}})$	± 0.17% of reading
$u(Q_{\mathrm{leakage,\ isobar-sec}})$	29×10^{-3} W
$u(Q_{\mathrm{leakage,\ JT-sec}})$	5.1×10^{-3} W
$u(\Delta E_{\mathrm{kinetic}})$	$+0.014$ kJ · kg^{-1} if $P_6 < 0.5$ MPa and gas phase; otherwise, ignorable
$u(z_i)$	± 0.00037 (or ± 0.037%)

where N is the number of individual variables, and $\partial \Delta h / \partial x_i$ is the partial derivative of Δh with respect to the individual variable, x_i.

Equation (1) consist of terms ($\dot{m}$, I, U) regarding the direct enthalpy increment measurement and terms (T, P, z) that have to be considered when calculating this enthalpy increment with an equation of state. From Eq. (1), the standard uncertainty of the measured isobaric enthalpy increment, $u(\Delta h)$, when comparing measurements with results from equations of state, is on average ± 0.08 kJ · kg^{-1}, equal to ± 0.22% of the enthalpy increment. The maximum values of the standard uncertainty is ± 0.124 kJ · kg^{-1} and ± 0.31% of the enthalpy increment.

A computer program that calculates the total uncertainties in the measured Δh is incorporated in a subroutine to the enthalpy database. Every test run on the calorimeter is linked to a certain calibration set. When some instrumentation on the calorimeter is changed or recalibrated, a new calibration set is made for the database, and the accuracy of each measurement can be calculated.

3.2. Measurement Results

The regions where the measurements have been performed are shown in the enthalpy pressure diagram in Fig. 3. The isobaric measurements cover the pressure levels 0.5, 1.0, 11.0, 13.0, and 14.0 MPa, at temperatures from 143.2 to 340.9 K.

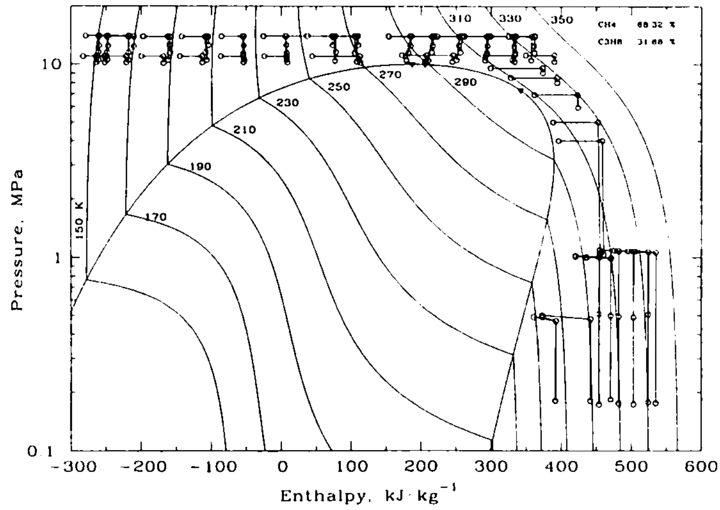

Fig. 3. Region of measurements performed on the 68.32% methane–31.68% propane mixture.

Table II. Enthalpy Increments, Δh, on a Mixture of 68.32% Methane and 31.68% Propane

Run No.	T_{in} (K)	T_{out} (K)	P_{in} (MPa)	P_{out} (MPa)	Δh_{exp} (kJ·kg^{-1})	Δh_{SRK} (kJ·kg^{-1})	$\Delta h_{exp}-\Delta h_{SRK}$ (kJ·kg^{-1})	$(\Delta h_{exp}-\Delta h_{SRK})/\Delta h_{exp}$ (%)
654	284.87	301.73	1.0186	1.0080	34.23	33.97	0.25	0.74
655	284.87	301.68	1.0116	1.0008	34.08	33.85	0.23	0.66
656	292.73	309.79	1.0047	0.9939	34.85	34.68	0.16	0.47
657	292.73	309.70	1.0006	0.9896	34.66	34.49	0.17	0.48
658	302.55	315.87	1.0942	1.0825	27.66	27.52	0.14	0.50
659	302.54	315.96	1.0917	1.0801	27.84	27.72	0.12	0.45
660	312.40	325.94	1.0885	1.0769	28.46	28.34	0.13	0.45
661	312.41	325.94	1.0859	1.0742	28.44	28.29	0.14	0.50
662	322.15	335.85	1.0804	1.0687	29.12	29.02	0.09	0.32
663	322.16	335.96	1.0787	1.0671	29.34	29.25	0.09	0.30
664	327.04	340.87	1.0735	1.0618	29.60	29.51	0.09	0.31
665	284.86	293.27	13.9984	13.9979	33.12	32.71	0.41	1.25
666	292.72	301.31	13.9849	13.9844	34.16	33.87	0.30	0.87
667	302.53	310.67	13.9720	13.9714	32.12	32.02	0.10	0.30
668	312.39	321.13	13.9626	13.9619	33.59	33.66	−0.07	−0.21
669	322.17	331.35	13.9562	13.9554	34.04	34.16	−0.13	−0.37
670	329.00	339.15	13.9509	13.9502	36.47	36.63	−0.16	−0.43
670B	284.86	292.92	13.9894	13.9889	31.85	31.33	0.52	1.64
671	292.72	301.24	13.9582	13.9577	33.90	33.62	0.28	0.81
672	302.53	311.55	13.9628	13.9622	35.51	35.46	0.05	0.13
673	312.40	321.28	13.9863	13.9855	33.90	34.19	−0.29	−0.87
674	322.18	331.90	13.9822	13.9813	35.66	36.11	−0.45	−1.26
675	329.01	339.37	13.9776	13.9768	36.86	37.38	−0.52	−1.42
676	329.01	338.08	13.9715	13.9705	32.32	32.80	−0.48	−1.49
677	322.18	330.74	13.9641	13.9632	31.39	31.86	−0.47	−1.51
678	312.40	320.67	13.9591	13.9583	31.55	31.87	−0.32	−1.01
679	302.55	310.49	13.9541	13.9535	31.29	31.29	−0.01	−0.02
680	292.73	300.61	13.9499	13.9493	31.45	31.08	0.37	1.18
681	284.91	292.75	13.9462	13.9457	31.16	30.57	0.59	1.89
682	284.90	292.87	11.1839	11.1832	35.76	35.53	0.24	0.66
683	292.75	301.33	11.1802	11.1794	37.22	38.11	−0.89	−2.40
684	312.36	322.79	11.1762	11.1752	39.24	40.95	−1.70	−4.33
685	327.01	338.53	11.1710	11.1699	39.31	40.57	−1.26	−3.21
686	307.44	327.12	9.5520	9.5511	70.84	74.30	−3.47	−4.89
687	309.39	328.15	8.5097	8.5083	62.66	65.52	−2.87	−4.57
688	309.39	329.43	6.9460	6.9445	61.47	61.22	0.26	0.42
689	304.48	328.83	5.0170	5.0147	65.09	63.95	1.14	1.75
690	299.57	324.97	4.0139	4.0107	63.73	62.25	1.49	2.33
999	252.89	273.27	14.0077	14.0074	69.87	72.39	−2.52	−3.61
1000	252.84	271.92	14.0051	14.0048	65.19	67.60	−2.40	−3.69
1001	252.85	272.69	14.0055	14.0051	67.97	70.36	−2.39	−3.51
1002	243.48	263.91	14.0046	14.0043	67.11	69.83	−2.71	−4.04
1003	243.47	264.33	14.0053	14.0050	68.66	71.37	−2.72	−3.96

Table II. *(Continued)*

Run No.	T_{in} (K)	T_{out} (K)	P_{in} (MPa)	P_{out} (MPa)	Δh_{exp} (kJ·kg^{-1})	Δh_{SRK} (kJ·kg^{-1})	$\Delta h_{exp} - \Delta h_{SRK}$ (kJ·kg^{-1})	$(\Delta h_{exp} - \Delta h_{SRK})/\Delta h_{exp}$ (%)
1004	243.48	263.16	14.0010	14.0006	64.66	67.19	−2.53	−3.92
1005	233.65	243.68	13.9991	13.9987	30.90	32.30	−1.40	−4.52
1006	233.66	243.74	13.9985	13.9981	31.13	32.46	−1.34	−4.30
1007	233.65	243.48	13.9958	13.9954	30.35	31.64	−1.29	−4.25
1008	214.11	224.44	13.9582	13.9577	29.49	31.11	−1.62	−5.49
1009	214.11	224.03	13.9559	13.9553	28.37	29.87	−1.51	−5.31
1010	214.10	224.61	13.9570	13.9564	30.12	31.68	−1.57	−5.20
1011	194.43	207.68	13.9106	13.9103	36.07	37.91	−1.84	−5.09
1012	194.40	206.12	13.9069	13.9063	31.95	33.45	−1.50	−4.70
1013	194.40	206.71	13.9084	13.9079	33.63	35.16	−1.53	−4.55
1014	174.70	187.31	13.9064	13.9059	33.28	34.40	−1.13	−3.39
1015	174.28	188.37	13.9085	13.9080	37.24	38.46	−1.22	−3.29
1016	174.31	188.28	13.9086	13.9081	36.97	38.12	−1.14	−3.09
1017	155.00	169.52	13.9069	13.9064	37.50	38.26	−0.76	−2.02
1018	154.93	166.65	13.9014	13.9006	30.22	30.80	−0.59	−1.94
1019	154.94	166.62	14.0378	14.0372	30.00	30.70	−0.70	−2.33
1020	143.22	155.12	14.0365	14.0358	30.26	30.79	−0.53	−1.74
1021	143.22	154.96	14.0350	14.0343	29.91	30.38	−0.47	−1.58
1022	143.22	155.47	14.0346	14.0340	31.21	31.69	−0.48	−1.52
1023	143.22	150.67	14.0344	14.0338	18.91	19.20	−0.29	−1.51
1024	143.21	150.28	14.0324	14.0316	17.99	18.24	−0.25	−1.39
1025	143.22	150.23	14.0320	14.0312	17.82	18.06	−0.24	−1.36
1026	253.24	270.72	11.0233	11.0222	63.27	68.46	−5.19	−8.20
1028	233.65	243.19	11.0240	11.0231	29.87	32.44	−2.57	−8.60
1029	214.11	224.32	11.0192	11.0185	29.67	31.84	−2.17	−7.31
1030	194.39	205.15	11.0169	11.0163	29.67	31.32	−1.65	−5.57
1031	174.72	185.99	11.0142	11.0137	29.89	31.14	−1.25	−4.19
1032	155.00	166.66	11.0027	11.0022	30.13	30.94	−0.81	−2.67
1033	143.29	155.22	11.0026	11.0019	30.52	31.10	−0.58	−1.89
1034	143.27	150.49	11.0034	11.0027	18.39	18.76	−0.37	−2.00
1035	255.23	291.38	0.5011	0.4798	68.46	68.86	−0.40	−0.58
1036	255.23	265.26	0.4910	0.4696	18.96	19.04	−0.08	−0.41
1037	248.37	265.44	0.4914	0.4701	32.00	32.02	−0.02	−0.05

The results of the isobaric enthalpy increment measurements are given in Table II. The temperatures T_{in} and T_{out} in the table are equal to T_2 and T_3, respectively, and the pressures P_{in} and P_{out} are equal to P_4 and P_5, respectively, referred to Fig. 1. The given enthalpy increment, Δh_{exp}, is the value given by $(U \times I)/\dot{m}$, corrected for the heat leakage through the power supply lines and the voltage measuring lines, and the heat generation in the power supply lines. The largest correction in the presented enthalpy increment measurements is 0.084% of the electrical heat input $(U \times I)$. Δh_{SRK} is the enthalpy increment calculated by the Soave–Redlich–Kwong (SRK) equation. The largest deviation between the calculations and the measurements is 8.6%.

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