TECHNICAL BRIEF

Thermodynamic Properties of Selected HFC Refrigerants

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Hydrofluorocarbon (HFC) refrigerants are receiving much attention as possible alternatives to replace ozone-depleting chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants. The flammability of a proposed new refrigerant is a major consideration in assessing its utility for a particular application. Enthalpy (or heat) of combustion (ΔH_{comb}), is one of the important parameters in assessing the flammability of a proposed new refrigerant. The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) considers the enthalpy of combustion together with the lower flammability limit (LFL) in classifying refrigerants as nonflammable, moderately flammable, or highly flammable (ASHRAE 1992). Also, combustion enthalpy is employed in the calculation of adiabatic flame temperatures and theoretically correlates with flammability limits. A related thermodynamic property, the Gibbs free energy of combustion (ΔG_{comb}), is a measure of the chemical force which drives the combustion reaction to equilibrium at constant temperature and pressure.

With few exceptions, enthalpies of combustion of HFCs have not been measured. Also, their standard enthalpies of formation (ΔH^o_f), Gibbs free energies of formation (ΔG^o_f), and absolute entropies (S^o) have not been determined. We therefore submit estimated thermodynamic functions for 21 HFCs which are known to have been synthesized and considered as potential refrigerants, either individually or as components in blends.

Table 1 provides standard (298.15 K, 101.3 kPa) Gibbs free energies of formation, enthalpies of formation, and absolute entropies for the 21 HFCs. With the exception of HFC-32 (R-32), these values were obtained using the group additivity method advanced by Domalski and Hearing (1993). This method is analogous to the group contribution methods of Yoneda and Benson commonly used by chemists and chemical engineers for deriving thermodynamic properties of ideal gases (Reid et al. 1987). In their work, Domalski and Hearing report that the discrepancy between their calculated values and experimental values of ΔH^o_f was less than ±8 kJ mol^{-1} for 71% of the 258 organic halogen compounds examined from the CHX and CHXO families. With respect to S^o, the discrepancy between calculated and experimental values was less than ±8 J mol^{-1} K^{-1} for 87% of the 258 compounds studied. Accordingly, enthalpies of formation and absolute entropies for the HFCs listed in Table 1 are believed to be similarly accurate. Possible exceptions are HFC-143a and HFC-143 for which reported measured values of ΔH^o_f are −744.6 ± 1.7 kJ mol^{-1} and −730.7 ± 20.8 kJ mol^{-1}, respectively (Kolesoz et al. 1965, Lacher et al. 1956). Values for R-32 in Table 1 are measured values, as reported in the Joint Army, Navy, Air Force Thermochemical Tables (JANAF 1985). Refrigerants marked with an asterisk (*) denote those which have been reported to exhibit flammability limits at room temperature and ambient pressure with spark or match ignition using the ASTM E 681-85 method (ASTM 1985).

Table 2 presents calculated molar ΔG_{comb} and ΔH_{comb} values for the HFCs at 298.15 K and 101.3 kPa. At this temperature, products resulting from complete com-

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bustion of the HFCs in air are the normal stable species CO_2, H_2O, HF, O_2, and N_2 specified from reaction stoichiometry. At product temperatures characteristic of most combustion systems (>1250 K), the distribution of equilibrium products would be more complex owing to dissociation of the stable species. Thermodynamic values provided in Table 2 are for complete oxidation of the HFCs to CO_2 and HF and are derived on the basis of all reactants and products being in the gaseous state. Hence, in the equations shown, H_2O is water vapor and HF is gaseous monomeric hydrogen fluoride.

For HFCs having a fluorine-to-hydrogen atom ratio >1, an additional source of hydrogen atoms must be provided as a reactant to achieve complete conversion of the HFC to CO_2 and HF. We have selected water vapor as being the most likely source of additional hydrogen atoms in a combustion scenario. However, it is important to note that, while a balanced chemical equation can be written for combustion of highly fluorinated HFCs to CO_2 and HF by including water vapor as a reactant, it may not be possible in practice to achieve the stoichiometric $HFC/O_2/H_2O$ mole ratio due to the saturation limits of water vapor in air. Therefore, for these highly fluorinated HFCs, we also tabulate ΔG_{comb} and ΔH_{comb} values for an alternative combustion reaction yielding carbonyl fluoride (COF_2) as one of the products. This alternative combustion is also feasible at 298.15 K and 101.3 kPa pressure, although less thermodynamically favored. COF_2 is a more probable product of combustion of HFCs with F:H ratios >1 than is diatomic fluorine, F_2. Formation of COF_2 from oxidation of such HFCs has been demonstrated indirectly in tests in which highly fluorinated HFCs have been evaluated as fire extinguishants.

Standard enthalpies of formation and absolute entropies for H_2O, CO_2, HF, O_2, and COF_2, which were used in calculating the combustion enthalpies and free energies, are provided as a footnote to Table 2.

Table 3 presents the free energy and enthalpy changes for these same combustion reactions on a mass of refrigerant basis. Additionally, the values are grouped by the number of carbon atoms in the refrigerant molecule, and within each group by increasing fluorine-to-hydrogen ratio. In this way, trends in the thermodynamic values with relative molecular mass, carbon number, extent of fluorination, and isomeric conformation may be more readily discerned.

It is worth repeating that combustion enthalpy is only one of several parameters useful in defining the flammability of a chemical. Many other considerations must be taken into account to arrive at a valid assessment of fire safety when using a potentially flammable refrigerant in a particular application.

REFERENCES

ASHRAE. 1992. Number Designation and Safety Classification of Refrigerants. *ANSI/ASHRAE Standard* 34-1992. Atlanta: ASHRAE.

ASTM. 1985. Standard Test Method for Concentration Limits of Flammability of Chemicals. *ASTM Standard* E681-85. Philadelphia: American Society for Testing and Materials.

Domalski, E.S., and E. D. Hearing. 1993. Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **22**, No. 4.

JANAF (Joint Army, Navy, Air Force). 1985. Thermochemical Tables, Third Edition, *J. Phys. Chem. Ref.* Data **14**, No. 1.

Kolesoz, V. P., A. M. Martynov, and S. M. Skuratov. 1965. *Rus. J. Phys. Chem.* **39**, 223.

Lacher, J. R., A. Kian Pour, F. Oetting, and J. D. Park,. 1956. *Trans. Faraday Soc.* **52**, 1500.

Reid, R. C., J. M. Prausnitz, and B. E. Poling. 1987. *The Properties of Gases & Liquids*, Fourth Edition. New York: McGraw-Hill Book Company.

Table 1. Estimated Gibbs free energies of formation (kJ mol^{-1}), enthalpies of formation (kJ mol^{-1}), and absolute entropies (J mol^{-1} K^{-1}) at 298.15 K and 101.3 kPa for several HFC refrigerants

Refrigerant No.	Formula	ΔG^o_f	ΔH^o_f	S^o
32*	CH_2F_2	–429.7	-452.1	246.7
161*	CH_3CH_2F	–213.9	-263.3	264.5
152*	CH_2FCH_2F	–392.8	–442.0	293.6
152a*	CH_3CHF_2	–445.4	–497.7	282.8
143*	CH_2FCHF_2	–616.2	–675.9	311.1
143a*	CH_3CF_3	–655.6	–716.2	305.5
134	CHF_2CHF_2	–854.4	–909.6	328.6
134a	CH_2FCF_3	–838.7	–895.0	325.0
125	CHF_2CF_3	–1069	–1129	342.5
254cb*	$CH_3CF_2CHF_2$	–825.1	–908.4	366.1
245ca*	$CH_2FCF_2CHF_2$	–1002	–1088	386.1
245cb*	$CH_3CF_2CF_3$	–1039	–1127	380.0
245fa*	$CHF_2CH_2CF_3$	–1060	–1151	373.0
236ca	$CHF_2CF_2CHF_2$	–1230	–1321	403.1
236cb	$CH_2FCF_2CF_3$	–1215	–1306	399.5
236ea	CHF_2CHFCF_3	–1241	–1334	389.7
236fa	$CF_3CH_2CF_3$	–1276	–1368	395.6
227ca	$CHF_2CF_2CF_3$	–1446	–1540	417.0
227ea	CF_3CHFCF_3	–1457	–1552	412.2
356mffm*	$CF_3CH_2CH_2CF_3$	–1267	–1389	434.9
338mccq	$CF_3CF_2CF_2CH_2F$	–1592	–1718	474.0

* Flammable at 298.15 K and 101.3 kPa by ASTM E681-85.

Table 2. ΔG_{comb} (kJ mol^{-1} HFC) and ΔH_{comb} (kJ mol^{-1} HFC) at 298.15 K and 101.3 kPa for several HFC refrigerants

Refrig. No.	Combustion Reaction	ΔG_{comb}	ΔH_{comb}
32	$CH_2F_2 + O_2 \rightarrow CO_2 + 2HF$	–511.6	–479.1
161	$C_2H_5F + 3O_2 \rightarrow 2CO_2 + HF + 2H_2O$	–1306	–1277
152	$C_2H_4F_2 + 5/2O_2 \rightarrow 2CO_2 + 2HF + H_2O$	–1172	–1125
152a	$C_2H_4F_2 + 5/2O_2 \rightarrow 2CO_2 + 2HF + H_2O$	–1119	–1069
143	$C_2H_3F_3 + 2O_2 \rightarrow 2CO_2 + 3HF$	–985.4	–862.7
143a	$C_2H_3F_3 + 2O_2 \rightarrow 2CO_2 + 3HF$	–954.3	–848.9
134	$C_2H_2F_4 + 3/2O_2 + H_2O \rightarrow 2CO_2 + 4HF$	–799.3	–710.8
	$C_2H_2F_4 + 3/2O_2 \rightarrow CO_2 + 2HF + COF_2$	–685.7	–631.0
134a	$C_2H_2F_4 + 3/2O_2 + H_2O \rightarrow 2CO_2 + 4HF$	–815.0	–725.4
	$C_2H_2F_4 + 3/2O_2 \rightarrow CO_2 + 2HF + COF_2$	–701.5	–645.7
125	$C_2HF_5 + O_2 + 2H_2O \rightarrow 2CO_2 + 5HF$	–629.0	–518.6
	$C_2HF_5 + O_2 \rightarrow HF + 2COF_2$	–402.0	–359.2
254cb	$C_3H_4F_4 + 3O_2 \rightarrow 3CO_2 + 4HF$	–1453	–1348
245ca	$C_3H_3F_5 + 5/2O_2 + H_2O \rightarrow 3CO_2 + 5HF$	–1320	–1194
	$C_3H_3F_5 + 5/2O_2 \rightarrow 2CO_2 + 3HF + COF_2$	–1207	–1115
245cb	$C_3H_3F_5 + 5/2O_2 + H_2O \rightarrow 3CO_2 + 5HF$	–1283	–1156
	$C_3H_3F_5 + 5/2O_2 \rightarrow 2CO_2 + 3HF + COF_2$	–1170	–1076
245fa	$C_3H_3F_5 + 5/2O_2 + H_2O \rightarrow 3CO_2 + 5HF$	–1262	–1132
	$C_3H_3F_5 + 5/2O_2 \rightarrow 2CO_2 + 3HF + COF_2$	–1148	–1052
236ca	$C_3H_2F_6 + 2O_2 + 2H_2O \rightarrow 3CO_2 + 6HF$	–1136	–988.9
	$C_3H_2F_6 + 2O_2 \rightarrow CO_2 + 2HF + 2COF_2$	–908.6	–829.5
236cb	$C_3H_2F_6 + 2O_2 + 2H_2O \rightarrow 3CO_2 + 6HF$	–1151	–1003
	$C_3H_2F_6 + 2O_2 \rightarrow CO_2 + 2HF + 2COF_2$	–923.9	–843.7
236ea	$C_3H_2F_6 + 2O_2 + 2H_2O \rightarrow 3CO_2 + 6HF$	–1125	–975.1
	$C_3H_2F_6 + 2O_2 \rightarrow CO_2 + 2HF + 2COF_2$	–898.8	–815.6
236fa	$C_3H_2F_6 + 2O_2 + 2H_2O \rightarrow 3CO_2 + 6HF$	–1090	–941.2
	$C_3H_2F_6 + 2O_2 \rightarrow CO_2 + 2HF + 2COF_2$	–863.1	–781.7
227ca	$C_3HF_7 + 3/2O_2 + 3H_2O \rightarrow 3CO_2 + 7HF$	–964.9	–796.4
	$C_3HF_7 + 3/2O_2 \rightarrow HF + 3COF_2$	–624.4	–557.2
227ea	$C_3HF_7 + 3/2O_2 + 3H_2O \rightarrow 3CO_2 + 7HF$	–954.2	–784.2
	$C_3HF_7 + 3/2O_2 \rightarrow HF + 3COF_2$	–613.7	–545.0
356mffm	$C_4H_4F_6 + 7/2O_2 + H_2O \rightarrow 4CO_2 + 6HF$	–1722	–1556
	$C_4H_4F_6 + 7/2O_2 \rightarrow 3CO_2 + 4HF + COF_2$	–1608	–1477
338mccq	$C_4H_2F_8 + 5/2O_2 + 3H_2O \rightarrow 4CO_2 + 8HF$	–1487	–1281
	$C_4H_2F_8 + 5/2O_2 \rightarrow CO_2 + 2HF + 3COF_2$	–1146	–1042

Note: To derive the ΔG_{comb} and ΔH_{comb} values of Table 2, the following standard enthalpies of formation (kJ mol^{-1}) and absolute entropies (J mol^{-1} K^{-1}) were used.

H_2O (g)	ΔH^o_f = –241.95	S^o = 188.8
CO_2 (g)	ΔH^o_f = –393.7	S^o = 213.7
HF (g)	ΔH^o_f = –268.7	S^o = 173.6
COF_2 (g)	ΔH^o_f = –609.5	S^o = 258.9
O_2 (g)	ΔH^o_f = 0	S^o = 205.1

Table 3. ΔG_{comb} (kJ kg^{-1} HFC) and $\Delta Hcomb$ (kJ kg^{-1} HFC) at 298.15 K and 101.3 kPa for HFC refrigerants.

Refrigerant No.	ΔG_{comb}	ΔH_{comb}
Carbon Number = 1		
32	−9 834	−9 209
Carbon Number = 2		
161	−27 178	−26 565
152	−17 738	−17 029
152a	−16 944	−16 186
143	−11 725	−10 920
143a	−11 265	−10 440
134 (#1)	−7 833	−6 966
134 (#2)	−6 721	−6 185
134a (#1)	−7 988	−7 110
134a (#2)	−6 875	−6 328
125 (#1)	− 5 241	− 4 321
125 (#2)	− 3 349	− 2 992
Carbon Number = 3		
254cb	−12 522	−11 612
245ca (#1)	−9 848	−8 911
245ca (#2)	−9 001	−8 316
245cb (#1)	−9 571	−8 620
245cb (#2)	−8 725	−8 025
245fa (#1)	−9 412	−8 445
245fa (#2)	−8 565	−7 851
236ca (#1)	−7 469	−6 505
236ca (#2)	−5 976	−5 456
236cb (#1)	−7 569	−6 598
236cb (#2)	−6 076	−5 549
236ea (#1)	−7 405	−6 414
236ea (#2)	−5 911	−5 365
236fa (#1)	−7 170	−6 191
236fa (#2)	−5 677	−5 142
227ca (#1)	−5 675	−4 684
227ca (#2)	−3 672	−3 277
227ea (#1)	−5 612	−4 612
227ea (#2)	−3 609	−3 205
Carbon Number = 4		
356mffm (#1)	−10 368	−9 372
356mffm (#2)	−9 685	−8 892
338mccq (#1)	−7 359	−6 340
338mccq (#2)	−5 673	−5 156

#1 and #2 refer to the alternative combustion reactions for HFCs with F:H ratios >1.
#1 indicates the reaction with water as a reactant.
#2 indicates the reaction without water as a reactant.