Ab Initio Calculations of Entropy and Heat Capacity of 1,1,1,2-Tetrafluoroethan (HFC-134a)

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Constant-pressure molar specific heat and entropy of 1,1,1,2-tetrafluoroethane at several temperatures were calculated by adopting *ab initio* molecular orbital theory and utilizing a double split valence type basis set. The calculated values for temperatures between -20.0 and 100.0 ℃ and a constant pressure of 101.3 kPa showed agreement with experimental results within 0.8 $\mathrm{Jmol^{-1}K^{-1}}$ for entropy and within 3.3 $\mathrm{Jmol^{-1}K^{-1}}$ for constant-pressure molar specific heat in the temperatures. However, some modification to the present approach is necessary for evaluating the pressure dependence of constant-pressure molar specific heat.

Since the ozone depletion theory was proposed, the use of many halogenated alkyls has been controlled by international protocols. Many efforts have been made to find new refrigerants that pose no risk of ozone depletion. Consequently, these works have provided several kinds of halogenated alkyls and alkyl mixtures for use as 2.5 generation alternative refrigerants[1] to replace conventional dichlorodifluoromethane (CFC-12) and chlorodifluoromethane (HCFC-22), which will be phased out by the years of 1996 and 2030, respectively.

In developing and designing such alternatives, heat capacity is one of the most important thermodynamic parameters because it is used to estimate a refrigerant's coefficient of performance (COP).[2] It is generally believed that the theoretical approach is a powerful tool,[3] especially for developing third generation refrigerant materials whose thermodynamic parameters have not been clarified experimentally.

In the present study, entropy per mole (S) and constant-pressure molar specific heat (C_p) of 1,1,1,2-tetrafluoroethane (HFC-134a) were calculated with *ab initio* molecular orbital theory[4,5] utilizing a D95V[6] basis set. C_p and S were obtained from formulas in reference 5 as

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\begin{aligned}
C_p &= T\,(\partial S/\partial T)_p \\
S &= S_{tr} + S_{rot} + S_{vib} + S_{el} - R\,(\ln N - 1) \\
S_{tr} &= R\,(3/2 + \ln(\pi MkT)^{3/2}(RT/P)) \\
S_{rot} &= R\,(3/2 + \ln(\pi v_a v_b v_c)^{1/2}/\sigma) \\
S_{vib} &= R\,\Sigma\, u_i\,(\exp(u_i) - 1)^{-1} - \ln(1 - \exp(-u_i)) \\
S_{el} &= R \ln \omega_{el}
\end{aligned}
$$

where v_a, v_b and v_c are $h^2/8\pi I_a$, $h^2/8\pi I_b$, $h^2/8\pi I_c$, respectively, σ is a symmetry number, I_a, I_b and I_c are moments of inertia for principal axes a, b and c, respectively, u_i is $h\lambda_i/kT$, λ_i is vibrational frequency, ω_{el} is a degeneracy number, and P is pressure. The Gaussian92 program[7] was used for total energy calculation, geometry optimization and vibrational frequency calculation.

HFC-134a was adopted in the present study because it is a prototype of the 2.5 generation alternative refrigerants[1] for air conditioners and refrigerators. However, the present theoretical approach can be easily applied to other hydrofluorocarbons (HFC's).

Calculated values of S and C_p at 20 ℃ intervals from -20.0 to 100.0 ℃ and at 101.3 kPa (1.0 atm) pressure are summarized in Table 1. Experimental values[8] are also presented in the table for comparison. These experimental values were estimated with a Modified Benedict-Webb-Rubin (MBWR) equation of state[8,9] whose parameters were obtained experimentally. The calculated values shown in Table 1 are in agreement with the experimental results within 0.8 $\mathrm{Jmol^{-1}K^{-1}}$ for S and within 3.3 $\mathrm{Jmol^{-1}K^{-1}}$ for C_p.

Table 1. Calculated values of entropy per mole (S) and constant-pressure molar specific heat (C_p) of 1,1,1,2-tetrafluoroethane (HFC-134a) at temperatures between -20.0 and 100.0 ℃, and at 101.3 kPa. Units are ℃ for T, and $\mathrm{Jmol^{-1}K^{-1}}$ for S and C_p

	Calculated			Experimental.[a]	
T	S	ΔS	C_p	ΔS	C_p
-20.0	302.6	0.0	77.7	0.0	81.0
0.0	308.6	6.0	81.6	6.2	83.4
20.0	314.5	11.9	85.1	12.2	86.2
40.0	320.1	17.5	88.3	18.0	89.2
60.0	325.6	23.0	91.1	23.6	92.3
80.0	331.0	28.4	93.6	29.1	95.4
100.0	336.2	33.6	95.8	34.4	98.5

[a] Reference 9.

Table 2. Calculated values of entropy per mole (S) and constant-pressure molar specific heat (C_p) of 1,1,1,2-tetrafluoroethane (HFC-134a) at pressures between 101.3 and 1000.0 kPa and at 40.0 ℃. Units are kPa for P, and $\mathrm{Jmol^{-1}K^{-1}}$ for S and C_p

	Calculated			Experimental[a]	
P	S	ΔS	C_p	ΔS	C_p
101.3	320.1	0.0	88.3	0.0	89.2
200.0	314.5	-5.7	88.3	-6.0	90.8
400.0	308.7	-11.4	88.3	-12.6	94.6
600.0	305.4	-14.8	88.3	-16.9	99.3
800.0	303.0	-17.2	88.3	-20.3	105.4
1000.0	301.1	-19.0	88.3	-23.4	113.7

[a] Reference 9.

Table 3. Contributions of translational, rotational, vibrational and electronic factors to entropy per mole (S) and constant-pressure specific heat (C_p) of 1,1,1,2-tetrafluoroethane (HFC-134a) at 40.0 ℃ and 101.3 kPa. Unit is $Jmol^{-1}K^{-1}$ for S and C_p

Factor	S	C_p
Translational	167.4	21.5
Rotational	111.7	12.9
Vibrational	41.0	53.9
Electronic	0.0	0.0
Total	320.1	88.3

The theoretically obtained pressure dependence of S and C_p of HFC-134a from 101.3 to 1000.0 kPa at 40.0 ℃ are summarized in Table 2 together with experimental values. Although the pressure dependence of S closely matches the experimental results within 4.4 $Jmol^{-1}K^{-1}$, some modification to the present approach seems necessary for evaluating the pressure dependency of C_p.

Table 3 summarizes the contributions of translational, rotational, vibrational and electronic factors to S and C_p of the HFC-134a molecule. According to the results given here, the contribution of molecular vibrations to C_p (61.0%) is the greatest among the factors mentioned above. It should be noted that the results given here are valid only for low pressures because the vibrational factors considered in our approach are estimated from molecular vibrations. For high pressures, the contribution of intermolecular interactions on vibrational factors should be considered to obtain more accurate theoretical values.

The present method will provide a useful tool in the developments of new refrigerants, especially of the third generation refrigerants whose thermodynamic parameters have not been found experimentally.

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References and Notes

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