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VAPOR PRESSURE MEASUREMENTS OF FERROCENE, MONO- AND 1,1′-DI-ACETYL FERROCENE

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ABSTRACT

By using different techniques the vapor pressure of ferrocene, mono-acetyl ferrocene and 1,1′-di-acetyl ferrocene was measured. The following pressure—temperature equations were derived

ferrocene $\log P(\text{kPa}) = 9.78 \pm 0.14 - (3805 \pm 46)/T$
mono-acetyl ferrocene $\log P(\text{kPa}) = 14.83 \pm 0.14 - (5916 \pm 48)/T$
1,1′-di-acetyl ferrocene $\log P(\text{kPa}) = 8.82 \pm 0.11 - (4289 \pm 44)/T$

By second- and third-law treatment of the vapor data the $\Delta H^\circ_{\text{sub},298} = 74.0 \pm 2.0$ kJ mole^{-1} for the sublimation process of ferrocene was calculated and compared with the literature data. For the sublimation enthalpy of mono- and 1,1′-di-acetyl ferrocene the values $\Delta H^\circ_{\text{sub},298} = 115.6 \pm 2.5$ kJ mole^{-1} and $\Delta H^\circ_{\text{sub},298} = 91.9 \pm 2.5$ kJ mole^{-1} were derived by second-law treatment. Thermal functions of these compounds were also estimated.

INTRODUCTION

Interest in the study of ferrocene's derivatives is mainly due to the wide utilization of these compounds as light-sensitive layers [1,2], polyester resins with improved flame resistance [3] and for the synthesis of polymers stable up to 750 K with semiconductor properties [4]. While the vapor pressure of ferrocene has been determined by several authors using different techniques [5—8], apparently no vapor pressure data are reported in the literature for mono- and 1,1′-di-acetyl ferrocenes. In view of this lack of experimental data we thought it useful to carry out vapor pressure measurements of these compounds by the torsion and Knudsen-effusion methods.

EXPERIMENTAL PROCEDURE AND RESULTS

A commercial ferrocene sample (Aldrich 96% pure) purified by sublimation under vacuum at 130°C was used in this study. The melting point (173.9 ± 0.5°C) was determined for testing the purity of the sublimate

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(m.p. = 174°C [9]). The mono-acetyl ferrocene (MAF) sample was synthesized according to the procedure suggested by Graham et al. [10]. The product was purified by chromatographic method using an alumina tower and benzene as diluent. 1,1′-Di-acetyl ferrocene (DAF) was prepared according to the procedure suggested by Rosenblum and Woodward [11]. The samples obtained were purified by sublimation under vacuum and their melting points (85.5 ± 0.5°C and 130.5 ± 0.5°C, for MAF and DAF, respectively), when compared with those reported in the literature (85—86°C and 130—131°C for MAF and DAF, respectively) [9], showed a good degree of purity. The vaporization experiments were carried out using two different effusion techniques.

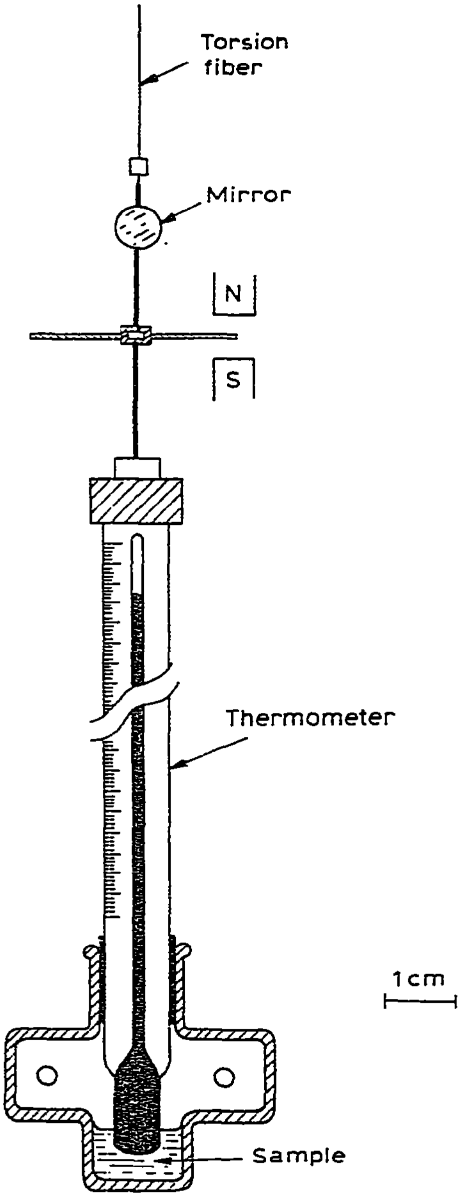

Fig. 1. Torsion-effusion apparatus.

TABLE 1

Vapor pressure of ferrocene and its third-law vaporization enthalpy

T (K)	α (deg.)	$P\ 10^3$ (kPa)	$-\Delta\ [(G^\circ_T - H^\circ_{298})/T]$ (J mole^{-1} K^{-1})	ΔH°_{298} (kJ mole^{-1})
Run 1				
297	7	1.00	151.95	73.59
301	9	1.29	151.95	73.97
302	10	1.43	151.95	73.97
307	14	2.01	151.91	74.30
308	16	2.29	151.87	74.18
310	18	2.57	151.87	74.39
314	26	3.72	151.83	74.34
316	39	5.58	151.83	73.76
319	50	7.16	151.74	73.76
321	57	8.18	151.74	73.88
322	62	8.88	151.78	73.92
323	65	9.30	151.70	73.97
324	72	10.34	151.66	73.92
325	85	12.16	151.66	73.72
327	98	13.98	151.62	73.76
328	104	14.89	151.62	73.80
331	130	18.64	151.58	73.84
333	149	21.38	151.49	73.88
334	158	22.60	151.49	73.97
337	223	31.92	151.54	73.63
339	282	40.33	151.41	73.42
			Average	73.9 ± 0.3 *
Run 2				
288	4	0.57	152.04	72.75
300	10	1.43	151.95	73.46
305	13	1.86	151.95	74.01
307	17	2.43	151.91	73.80
309	18	2.57	151.91	74.13
314	32	4.58	151.83	73.80
318	47	6.73	151.78	73.73
320.5	62	8.88	151.74	73.55
321	66	9.45	151.74	73.51
323	81	11.55	151.70	73.38
324	87	12.46	151.66	74.26
326	105	15.00	151.62	73.34
328	128	18.34	151.62	73.26
330	153	21.32	151.58	73.21
333	192	27.46	151.49	73.21
337	243	34.75	151.45	73.42
339	273	39.11	151.41	73.51
341	303	43.37	151.37	73.63
342	318	45.49	151.32	73.67
344	354	50.66	151.28	73.80
346	377	54.01	151.24	74.01
347	383	54.82	151.20	74.18
348	393	56.24	151.20	74.30
351	453	64.85	151.70	74.51
353	631	90.38	151.07	73.97
			Average	73.7 ± 0.4 *

* The error is the standard deviation.

Torsion method

The method and the experimental apparatus are reported in detail in previous works [12,13]. At each temperature of the effusion cell, the vapor pressure of the analyzed sample was derived from the torsion angle, α, of the Ni—Pt fiber [$(6 \times 0.6) \times 10^{-3}$ cm] to which the cell was suspended, by the well-known equation

$$P(\text{atm}) = 2K\alpha(a_1b_1f_1 + a_2b_2f_2)^{-1} = K^\circ\alpha$$

where K° is a constant that takes into account the geometrical constants of

TABLE 2

Vapor pressure of mono-acetyl ferrocene and di-acetyl ferrocene

MAF			DAF		
T (K)	α (deg.)	$P\ 10^3$ (kPa)	T (K)	α (deg.)	$P\ 10^3$ (kPa)
Run 1					
333	8	1.14	363	8	1.13
338	15	2.15	367	11	1.58
342	24	3.43	373	15	2.15
344	31	4.44	374	17	2.43
346	38	5.44	377	20	2.87
347	44	6.30	382	30	4.30
348.5	50	7.16	384	34	4.86
350	59	8.45	386	36	5.16
351	64	9.16	388	46	5.58
353	89	12.77	394	69	7.87
355	105	15.00	398	79	11.34
			401	93	13.38
			404	115	16.41
Run 2					
329	5	0.72	360	7	0.72
336	11	1.58	367	9	1.29
338	14	2.00	371	13	1.86
340	19	2.71	375	16	2.29
341	23	3.29	378	20	2.87
344	30	4.30	380	22	3.15
346	37	5.30	381	24	3.44
347	41	5.87	383	30	4.30
349	55	7.87	385	36	5.16
351	69	9.88	388	38	5.44
353	79	11.34	389	42	6.02
354	91	13.07	390	45	6.44
355	101	14.49	391	48	6.87
357	122	17.43	392	52	7.45
358	131	18.75	393	56	8.01
			394	60	8.59
			398	74	10.64
			404	115	16.41

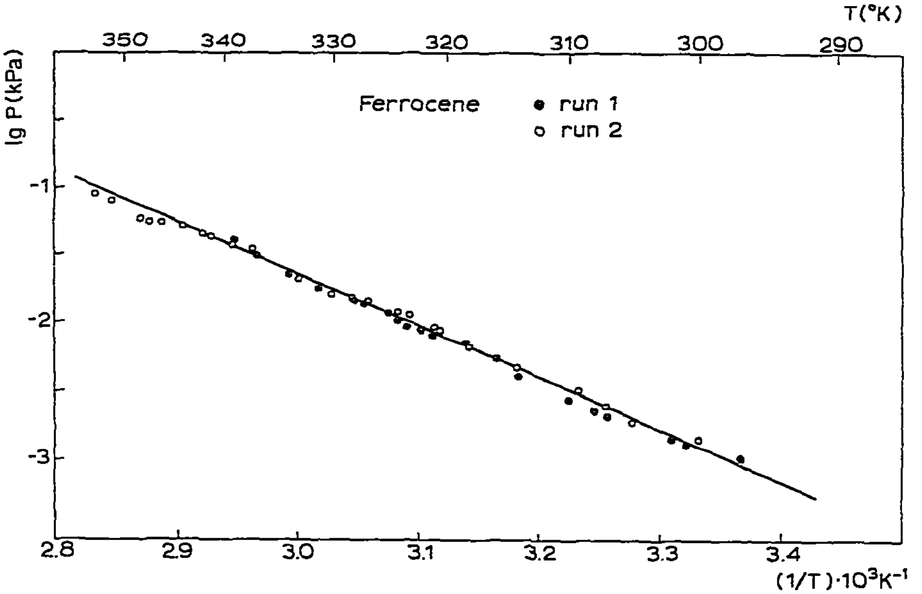

Fig. 2. Experimental vapor pressure of ferrocene.

the cell and the torsion constant of the Ni—Pt fiber. In this study a glass effusion cell was used and its temperature measured by a calibrated thermometer inserted into the cell (as reported in Fig. 1). The calibration factor of the used assembly, $K^\circ = (1.432 \pm 0.073) \times 10^{-4}$ kPa $\deg^{-1}$, was deduced by the vaporization of standard substances, e.g. mercury and naphthalene, for which the vapor pressures are well known [14,15]. The vapor pressure data

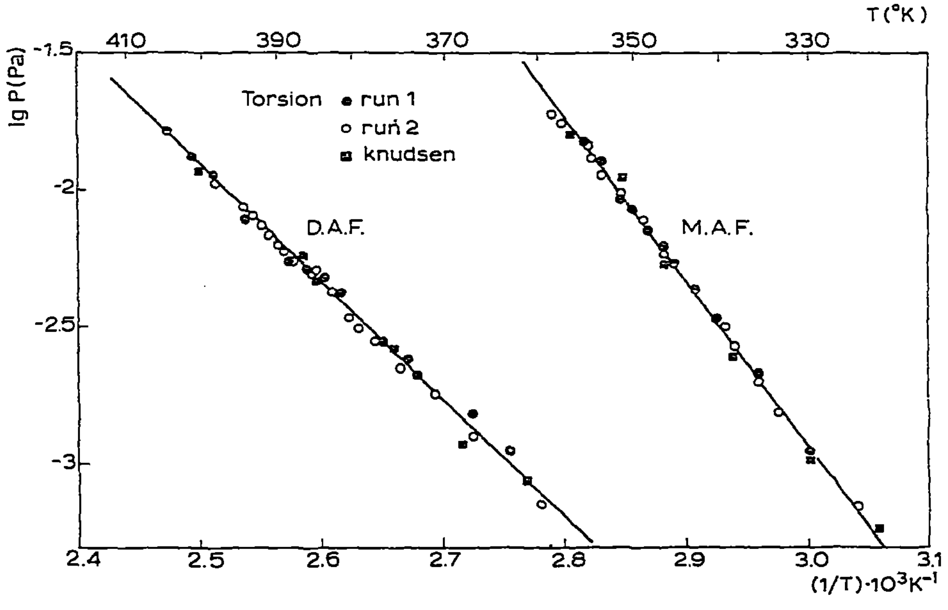

Fig. 3. Experimental vapor pressure of mono-acetyl ferrocene (MAF) and di-acetyl ferrocene (DAF).

TABLE 3

Summary of the pressure—temperature equations of solid ferrocene, mono-acetyl ferrocene and 1,1′-diacetyl ferrocene

Compound	Method	Run	T (K)	$\log P(\text{kPa}) = A - B/T$		ΔH°_T (kJ mole^{-1})	ΔH°_{298} (kJ mole^{-1})	
				A	B		Second law	Third law
Ferrocene	Torsion	1	297—339	10.14 ± 0.15	3926 ± 46	75.1 ± 0.8	76.5 ± 0.8	73.9 ± 0.3
		2	288—353	9.45 ± 0.14	3695 ± 46	70.7 ± 0.8	71.9 ± 0.8	73.7 ± 0.4
MAF	Torsion	1	333—355	15.06 ± 0.14	5991 ± 50	114.6 ± 0.8	116.6 ± 0.8	
	Torsion	2	329—358	14.69 ± 0.14	5866 ± 48	112.0 ± 0.8	114.1 ± 0.8	
	Knudsen		327—356	14.79 ± 0.57	5901 ± 197	112.9 ± 4.0	115.0 ± 4.0	
DAF	Torsion	1	363—404	8.29 ± 0.13	4078 ± 49	78.2 ± 0.8	87.8 ± 0.8	
	Torsion	2	360—404	9.14 ± 0.10	4413 ± 39	84.4 ± 0.8	94.1 ± 0.8	
	Knudsen		361—400	9.03 ± 0.37	4374 ± 142	83.6 ± 2.5	93.2 ± 2.5	

Note: all the associated errors are standard deviations.

of ferrocene, MAF and DAF samples, determined by this method, are reported in Tables 1 and 2 and plotted as $\log_{10}P$ vs. $1/T$ in Figs. 2 and 3. Least-squares treatment of the data gives the pressure—temperature equations summarized in Table 3.

Knudsen-effusion technique

This technique was used to study the MAF and DAF compounds. The vapor pressure values of these samples were determined by measuring their weight loss when heated in a Knudsen cell, through the equation

$$P(\text{kPa}) = 2.29K'm(T/M)^{1/2}(S\ \Delta t)^{-1}$$

where m is the mass of the sample effused from the cell in time Δt, S and K' are the area of the hole and Clausing's factor, respectively [16], and M is the molar weight of the vapor, the employed assembly is reported in Fig. 4. Two stainless steel cells with different effusion holes (1.0 and 1.5 mm in diameter) were used. The necessary calibration factors, obtained through the vaporization of a standard element (mercury), were found in agreement within 5% with the value calculated from geometrical evaluation. The vapor

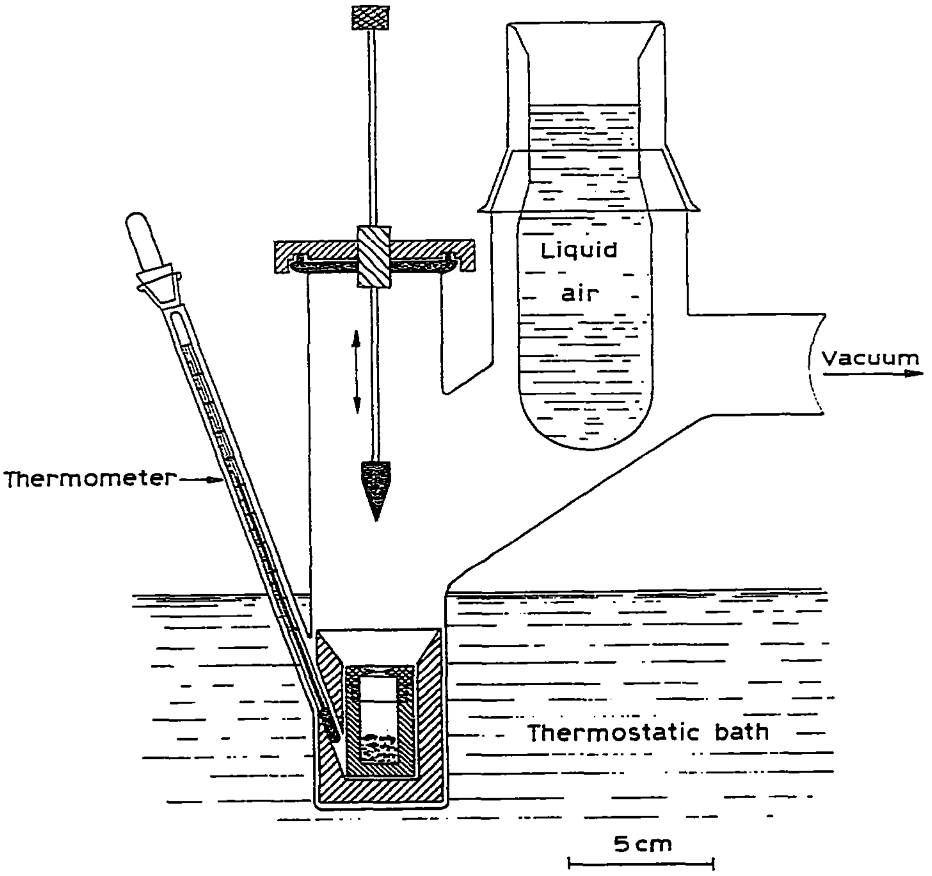

Fig. 4. Knudsen-effusion apparatus.

TABLE 4

Vapor pressure of MAF and DAF determined by the Knudsen-effusion technique

Sample	Cell	Diameter eff. hole (mm)	T (K)	m ($\times 10^{-2}$) (g)	Δt (sec.)	P (kPa)
MAF	L	1.50 ± 0.05	327	2.129	7200	6.11×10^{-4}
	S	1.00 ± 0.05	333	2.692	12180	1.03×10^{-3}
	S	1.00 ± 0.05	340	3.720	7200	2.48×10^{-3}
	S	1.00 ± 0.05	347	4.029	3600	5.37×10^{-3}
	L	1.50 ± 0.05	351	9.560	1800	1.13×10^{-2}
	S	1.00 ± 0.05	356	8.735	2700	1.57×10^{-2}
DAF	L	1.50 ± 0.05	361	3.186	7200	8.82×10^{-4}
	S	1.00 ± 0.05	368	2.355	9000	1.19×10^{-3}
	S	1.00 ± 0.05	376	4.190	7200	2.66×10^{-3}
	L	1.50 ± 0.05	385	6.745	3000	4.63×10^{-3}
	S	1.00 ± 0.05	387	6.777	5400	5.83×10^{-3}
	S	1.00 ± 0.05	400	9.074	3600	1.19×10^{-2}

pressure data measured at each experimental temperature are reported in Table 4. The results of the least-squares analysis of the data and the pressure—temperature equation are reported in Table 3 and Fig. 3, respectively.

CONCLUSION

From the vapor pressure—temperature equations derived from both techniques the following equations for ferrocene, MAF and DAF were selected

$$\text{ferrocene} \quad \log P(\text{kPa}) = 9.78 \pm 0.14 - (3805 \pm 46)/T \qquad (1)$$

$$\text{MAF} \quad \log P(\text{kPa}) = 14.83 \pm 0.14 - (5916 \pm 48)/T \qquad (2)$$

$$\text{DAF} \quad \log P(\text{kPa}) = 8.82 \pm 0.11 - (4289 \pm 44)/T \qquad (3)$$

The slopes and the intercepts were calculated by weighting, proportionally to the number of points, the corresponding values determined in each run. The associated errors are the standard deviations.

By a third-law treatment of the vapor pressure data, the sublimation enthalpy of ferrocene at 298 K was calculated at each temperature and the obtained values are reported in Table 1. The necessary free energy functions, $(G^\circ_T - H^\circ_{298})/T$, were taken from the literature [17,18]. Very good agreement was found between the average third-law $\Delta H^\circ_{\text{sub},298} = 73.8 \pm 0.4$ kJ mole^{-1} and the corresponding second-law $\Delta H^\circ_{\text{sub},298} = 74.1 \pm 0.8$ kJ mole^{-1} derived from the slope of eqn. (1) and by using the enthalpic functions reported in the literature [17,18].

The average value $\Delta H^\circ_{\text{sub},298} = 74.0 \pm 2.0$ kJ mole^{-1}, where the error represents an overall estimated error, is compared in Table 5 with the results reported in the literature. The very satisfactory agreement can be considered as proof of the reliability of the instrument constant values and that equili-

TABLE 5

Comparison of vapor pressure equations and sublimation enthalpies of ferrocene

Ref.	T (K)	Method	Pressure—temperature equation	ΔH_T° (kJ mole^{-1})	ΔH_{298}° (kJ mole^{-1})
5	357—456	Quartz Bourdon Gauge	$\log P_{mm} = 10.27 - 3680/T$	70.46	
6	323—367	Knudsen effusion	$\log P_{mm} = 12.4 - 4350/T$	83.26	85.19
7	295—303	Knudsen effusion	$\log P_{mm} = 10.403 - 4001/T$		76.57 ± 0.13
7	295—303	Knudsen Hiby factor	$\log P_{mm} = 9.805 - 3830/T$		73.35 ± 0.42
7	295—302	Thermisistor Gauge			72.38 ± 1.26
8	293—306	Knudsen effusion	$\log P_{mm} = 28.17 - 4581/T - 6.04 \log T$	72.72 ± 0.54	
This work	288—353	Torsion effusion	$\log P_{kPa} = (9.78 \pm 0.14) - (3805 \pm 46)/T$		74.0 ± 2.0

TABLE 6

Thermodynamic properties of mono-acetyl ferrocene and 1,1′-di-acetyl ferrocene

Solid			Gas	
T (K)	$(H^\circ_T - H^\circ_{298})$ * (J mole^{-1})	$-(G^\circ_T - H^\circ_{298})/T$ *** (J mole^{-1} K^{-1})	$(H^\circ_T - H^\circ_{298})$ ** (J mole^{-1})	$-(G^\circ_T - H^\circ_{298})/T$ ** (J mole^{-1} K^{-1})
Mono-acetyl ferrocene				
298.15		144.47		397.81
300	527	144.52	456	397.81
310	3008	144.93	2929	397.98
320	5673	145.48	5125	398.27
330	8447	146.06	7326	398.65
340	11334	146.90	9219	399.28
350	14330	147.99	12008	400.16
360	17443	149.03	13916	401.04
370	20661	150.21	16113	402.04
380	23995	151.50	18309	403.17
390	27443	152.97	20510	404.47
400	30999	154.72	22405	406.10
1,1′-Di-acetyl ferrocene				
298.15		240.50		403.80
300	540	240.71	452	403.80
310	3523	241.84	2820	403.88
320	6611	243.51	5192	404.13
330	9803	244.47	7514	404.59
340	13100	245.98	9786	405.22
350	16498	247.61	12058	406.02
360	20000	249.24	14217	406.89
370	23602	251.08	16376	407.98
380	27309	252.92	18468	409.15
390	31121	254.72	20493	410.28
400	35037	256.90	22518	411.83

* See ref. 20.

** See ref. 19.

*** Calculated in this work.

librium conditions existed within the used cells. As concerns the ferrocene derivatives, the second-law $\Delta H^\circ_{\text{sub},343} = 113.4 \pm 0.8$ kJ mole^{-1} and $\Delta H^\circ_{\text{sub},382} = 82.0 \pm 0.8$ kJ mole^{-1} for MAF and DAF, respectively, were derived.

By using the enthalpic functions measured by Bencivenni [19] for the gaseous phase and by Tomassetti and D'Ascenzo [20] for the solid phase (see Table 6), the sublimation enthalpies at 298 K, $\Delta H^\circ_{\text{sub},298} = 115.6 \pm 2.5$ kJ mole^{-1} and $\Delta H^\circ_{\text{sub},298} = 91.9 \pm 2.5$ kJ mole^{-1} were obtained for MAF and DAF, respectively. Also in this case the associated errors are overall estimated errors. From these values and the experimental vapor pressure data, and the known free energy function of the gaseous phase [19], the free energy functions of the solid phase were calculated by the third-law equation

$$[(G^\circ_T - H^\circ_{298})/T]_{\text{sol}} = [(G^\circ_T - H^\circ_{298})/T]_{\text{gas}} + \Delta H^\circ_{\text{sub},298}/T + R \ln K_p$$

The obtained values are summarized in Table 6.

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