Enthalpy Change on Vaporization of Aqueous and Methanolic Formaldehyde Solutions

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A physicochemical model for vapor-liquid equilibrium in multicomponent formaldehyde-containing mixtures (Maurer, 1986; Hasse et al., 1990; Hasse and Maurer, 1991a) is extended to describe enthalpy changes upon vaporization. Predicted enthalpy changes are compared with new experimental results. The measurements were carried out with a thin-film evaporator flow-calorimeter (Liu and Maurer, 1991). More than 80 experimental data points for mixtures of formaldehyde + water and formaldehyde + methanol + (small amounts of water) are reported. The data cover the temperature range from 323 to 363 K (formaldehyde + water) and 312 to 347 K (formaldehyde + methanol) at liquid phase formaldehyde mole fractions up to about 0.3 (formaldehyde + water) and 0.6 (formaldehyde + methanol). Comparisons between predicted and experimental results for the enthalpy change reveal deviations of only a few percent. Further improvements are achieved by fitting some model parameters, which originally were estimated from noncalorimetric data.

Introduction

Due to its extremely high reactivity, formaldehyde is almost never prepared as a pure substance, but is produced, stored, and processed in aqueous or methanolic solutions. The concentration of monomeric formaldehyde in these solutions is very low, as formaldehyde is dissolved mainly chemically, forming polymers with water and methanol (Walker, 1964; Ullmann, 1988). The chemical reactions have an essential influence on the thermodynamic properties of aqueous and methanolic formaldehyde solutions. The most important chemical reactions in these solutions are:

- Formation of methylene glycol (MG)

$$CH_2O + H_2O \rightleftharpoons HO(CH_2O)H$$

- Formation of polyoxymethylene glycols (MG_n)

$$HO(CH_2O)_{n-1}H + HO(CH_2O)H \rightleftharpoons HO(CH_2O)_nH + H_2O \quad (n \geq 2)$$

- Formation of hemiformal (HF)

$$CH_2O + CH_3OH \rightleftharpoons CH_3O(CH_2O)H$$

- Formation of polyoxymethylene hemiformals (HF_n)

$$CH_3O(CH_2O)_{n-1}H + CH_3O(CH_2O)H \rightleftharpoons CH_3O(CH_2O)_nH + CH_3OH \quad (n \geq 2).$$

For separation process design reliable models for fluid properties are needed. For formaldehyde-containing mixtures such a model is available for the vapor-liquid equilibrium (Maurer, 1986; Hasse et al., 1990; Hasse and Maurer, 1991a). That physicochemical model can be extended in a straightforward manner to describe enthalpy differences. The resulting enthalpy model has already been applied for the calculation of the heat of dilution of formaldehyde-containing solutions (Hasse and Maurer, 1992), but predictions of the enthalpy change upon vaporization of formaldehyde-containing solutions with this model could not be checked, due to the almost complete lack of experimental data. The only sources (quoting experimentally determined numbers for the heat of solution

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of formaldehyde gas in water and methanol respectively) are over 60 years old (Delépine, 1897; Walker, 1933). This situation may be due to the fact that measurements of caloric properties related to the vapor-liquid phase transition of formaldehyde-containing mixtures require special techniques. Conventional calorimeters (for example, Majer et al., 1989) cannot be used, as slow chemical reactions occur in these mixtures (cf. Hasse and Maurer, 1991b) and as evaporation can result in the precipitation of solids when the solubility limit of formaldehyde polymers is exceeded.

This article reports on new experimental data for the enthalpy change upon partial vaporization of aqueous and methanolic formaldehyde mixtures at temperatures between 323 and 363 K (formaldehyde + water) and 312 and 347 K (formaldehyde + methanol) at pressures below 100 kPa and formaldehyde concentrations of up to about 0.3 mol/mol (formaldehyde + water) and 0.6 mol/mol (formaldehyde + methanol) as well as the prediction and correlation of the data with the physicochemical model mentioned above.

Measurements

The measurements were carried out with a thin-film evaporator flow-calorimeter (cf. Figure 1) especially designed for the measurement of enthalpy changes of chemical reactive mixtures upon vaporization. A similar though noncalorimetric technique has been successfully applied to the measurement of vapor-liquid equilibria in formaldehyde-containing mixtures (Maurer, 1986; Hasse et al., 1990). The calorimeter as well as results of test runs on pure water have been described elsewhere (Liu, 1991; Liu and Maurer, 1992).

A rotating coil (b) spreads the liquid feed (a) as a thin-film on the inner surface of a vertical thin-walled calorimeter tube (c). Power, supplied by an electrical heater (d) soldered onto the outer surface of tube (c), causes a partial vaporization of the liquid (mass of vapor phase ≤ 8% of mass of feed). The resulting vapor and liquid phase are separated. They leave the calorimeter through the vapor line (f) at the vapor phase outlet (i) and through the liquid line (h) at the liquid phase outlet (j). The vapor line is protected against entrained droplets by cap (e), the liquid line is formed as a siphon so that no vapor can pass. The two phases are collected in two weighing condensers. The pressure is transferred to the calorimeter from a helium filled pressure regulator system through the condensers. The temperatures of the liquid feed and of the saturated vapor leaving the calorimeter, the pressure and the electric power are measured. The data are collected and stored with a personal computer.

The calorimeter tube is mounted into a cylindrical jacket evacuated to about 10^{-4} Pa to avoid convective heat loss. To reduce heat loss by radiation a polished aluminum shield surrounds the calorimeter tube. Furthermore, the whole calorimeter is immersed in a thermostated bath which also contains a heat exchanger used to thermostat the liquid mixture before entering the calorimeter (residence time about 60 min).

The pressure was measured with a membrane pressure transducer with an accuracy of about 0.03 kPa. The temperatures were measured with an accuracy of better than 0.01 K by two platinum resistance thermometers, one in the thermostated bath near calorimeter entry, the other in the vapor line leaving the calorimeter. The electric energy was measured with an accuracy of 0.015%. The masses of samples (typically about 3 g vapor and 80 g liquid for aqueous solutions, and about 5 g vapor and 50 g liquid for methanolic solutions) were determined with an accuracy of better than 0.01 g (vapor) and about 0.05 g (liquid).

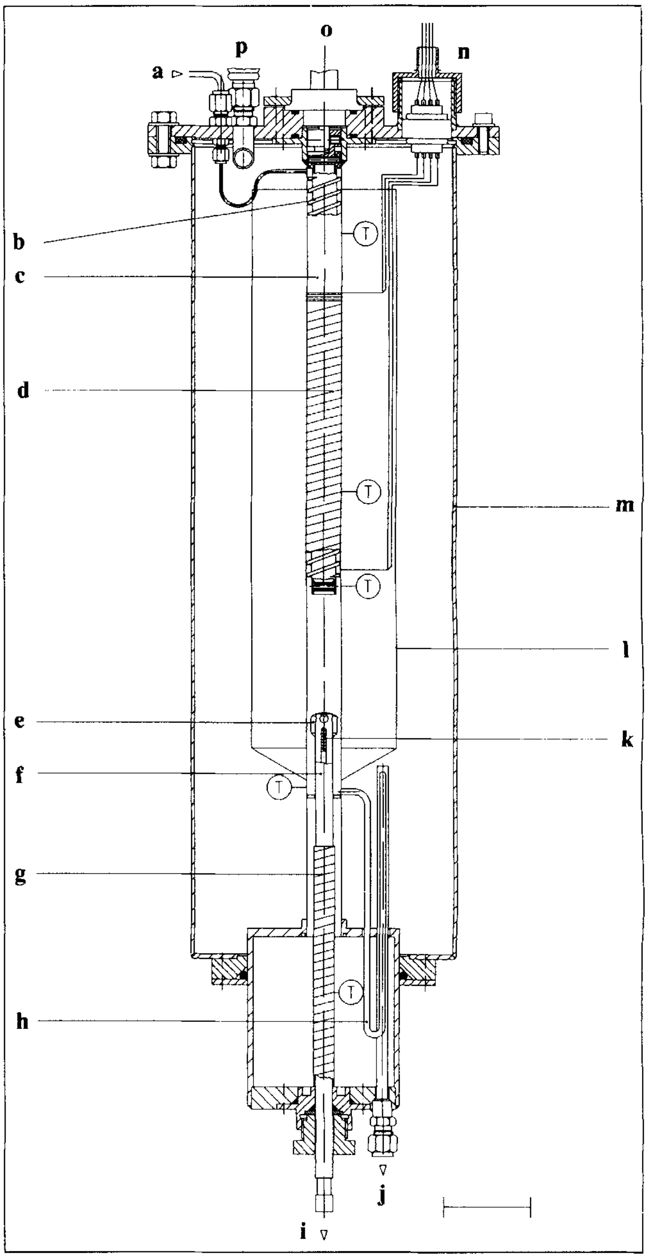

Figure 1. Calorimeter.

(a) calorimeter inlet; (b) coil; (c) calorimeter tube; (d) electric heater; (e) LID; (f) vapor line; (g) heater for vapor line; (h) liquid line and siphon; (i) vapor outlet; (j) liquid outlet; (k) platinum resistance thermometer for measuring the saturation temperature; (l) heat protection shield; (m) vacuum jacket; (n) to electrical heater and to determine supplied energy; (o) magnetic clutch; (p) vacuum connection; T, thermocouple element.

Aqueous and methanolic formaldehyde mixtures were prepared by dissolving paraformaldehyde in water and methanol at elevated temperatures and separating solid residues by filtration. Therefore, the liquid methanolic formaldehyde mixtures also contained about 3-4 mol % of water. All chemicals except water (deionized at the University of Kaiserslautern) were purchased from Merck, Darmstadt, Germany, or Riedel de Haen, Seelze, Germany in the best available quality and used without further purification. Gas chromatographic analysis showed only trace amounts of impurities of the samples (less than about 0.1 mass percent).

Formaldehyde concentrations were determined with relative uncertainties of less than 2% by applying the sodium sulfite method (Walker, 1964). In methanolic formaldehyde mixtures the small amount of water was determined by Karl-Fischer-titration. As it is well known, the presence of aldehydes disturbs water analysis using normal Karl-Fischer-reagents, because there are reactions between aldehydes and methanol (solvent for the normal Karl-Fischer-titration) which yield water. This, however, is not likely to disturb the analysis of water in methanolic formaldehyde solutions, where already the sample contains considerable amounts of methanol. This was checked by comparing analytical results for water concentrations obtained with normal (HYDRANAL-Titrant 2 NH and HYDRANAL-Solvent, Riedel de Haen, Seelze, Germany) and special (HYDRANAL-Composite 5 K and HYDRANAL-Composite K) Karl-Fischer-reagent couples. The special couple is designed to avoid problems with aldehyde-containing solutions. The results of the analysis with both reagent couples agreed within about 5% (relative deviation) which is about the normal scattering of the analytical results with this method. Another problem with this analytical method could arise from the water bound in methylene glycol or polyoxymethylene glycols. This amount is, however, for the samples analyzed with the Karl-Fischer titration in this work rather small. Typically less than 20% of the water is bound in formaldehyde-water reaction products. Furthermore, tests were carried out, by adding known amounts of water to methanolic formaldehyde solutions. Results of water analysis of these samples agreed with the numbers calculated using the mass of the added water, typically within 8% (relative deviation). We therefore estimate the uncertainty of the water analysis to be about 8% (relative deviation).

As the amounts of mass and the compositions of the coexisting phases leaving the calorimeter as well as the composition of the liquid feed were determined, mass balances provided a means to check the analysis. No discrepancies exceeding the given analytical uncertainties were found.

Model

The physicochemical vapor-liquid equilibrium model for multicomponent formaldehyde-containing mixtures of Maurer (1986) can be extended in a straightforward manner to enthalpy calculations. Figure 2 shows the basic assumptions for the system formaldehyde, water, and methanol. The formation of methylene glycol *MG*, hemiformal *HF*, polyoxymethylene glycols MG_n and polyoxymethylene hemiformals HF_n are taken into account. Due to the low vapor-pressures of the polyoxymethylene glycols and polyoxymethylene hemiformals, their presence in the gas phase is neglected. As the total pressure in formaldehyde processing units rarely exceeds 0.5 MPa, the gas phase is treated as a mixture of ideal gases. The influence of pressure on the liquid phase partial molar enthalpies is neglected. Nonidealities in the liquid phase are taken into consideration by using the UNIFAC group-contribution method (Gmehling et al., 1982). For normalization purposes, the molar enthalpies of the pure liquid components formaldehyde, water and methanol at $T^\theta = 273.15$ K are set to zero:

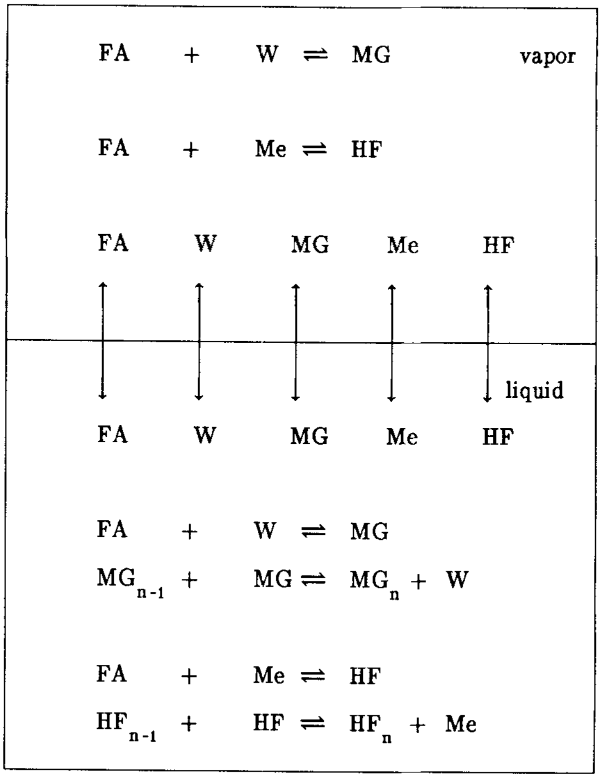

Figure 2. Vapor-liquid equilibrium in the formaldehyde + water + methanol system.

$$H^*_m(i,l,T^\theta) = 0. \qquad i = FA, W, Me \qquad (1)$$

The molar enthalpies of pure liquid formaldehyde, water and methanol at temperature *T* are calculated from molar heat capacities of the pure liquids $C^*_{p,m}\ (i,l,T)$:

$$H^*_m(i,l,T) = \int_{T^\theta}^{T} C^*_{p,m}(i,l,T)dT. \qquad i = FA, W, Me \qquad (2)$$

The molar enthalpies of these components in the vapor phase are calculated using the molar enthalpy of vaporization $\Delta_{\mathrm{vap}}H^*_m\ (i,T^\theta)$ at temperature T^θ and the molar heat capacities of the pure gases $C^*_{p,m}\ (i,g,T)$:

$$H^*_m(i,g,T) = \Delta_{\mathrm{vap}}H^*_m(i,T^\theta) + \int_{T^\theta}^{T} C^*_{p,m}(i,g,T)dT. \qquad (3)$$

$$i = FA, W, Me$$

The molar enthalpies of pure gaseous methylene glycol and hemiformal are calculated from the reaction enthalpies $\Delta_r H_m(MG,g,T)$ and $\Delta_r H_m(HF,g,T)$ for the formation of methylene glycol and hemiformal respectively in the vapor phase:

$$H^*_m(MG,g,T) = H^*_m(FA,g,T) + H^*_m(W,g,T) + \Delta_r H_m(MG,g,T) \qquad (4)$$

$$H^*_m(HF,g,T) = H^*_m(FA,g,T) + H^*_m(Me,g,T) + \Delta_r H_m(HF,g,T). \qquad (5)$$

With given numbers for the enthalpy of the pure gaseous components, the enthalpies of pure liquid methylene glycol and hemiformal are calculated from:

$$H^*_m(MG,l,T) = H^*_m(MG,g,T) - \Delta_{\text{vap}} H^*_m(MG,T) \qquad (6)$$

$$H^*_m(HF,l,T) = H^*_m(HF,g,T) - \Delta_{\text{vap}} H^*_m(HF,T). \qquad (7)$$

With the reaction enthalpies for the formation of polyoxymethylene glycol $\Delta_r H_m(MG_n,l,T)$ and polyoxymethylene hemiformal $\Delta_r H_m(HF_n,l,T)$ in the liquid phase, the molar enthalpies of the pure liquid polymers are given by:

$$H^*_m(MG_n,l,T) = H^*_m(MG_{n-1},l,T) + H^*_m(MG,l,T) - H^*_m(W,l,T) + \Delta_r H_m(MG_n,l,T) \qquad (8)$$

$$H^*_m(HF_n,l,T) = H^*_m(HF_{n-1},l,T) + H^*_m(HF,l,T) - H^*_m(Me,l,T) + \Delta_r H_m(HF_n,l,T). \qquad (9)$$

Finally the molar enthalpy of the gaseous and liquid mixture are calculated from:

$$H_m(g,T,\underline{y}) = \sum_i y_i H^*_m(i,g,T). \qquad (10)$$

$$H_m(l,T,\underline{x}) = \sum_i x_i \{H^*_m(i,l,T) + H^E_m(i,T,\underline{x})\}. \qquad (11)$$

Table 1. Pure Component Data for Formaldehyde, Water and Methanol

Heat Capacity: $C_{p,m}{}^*/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = \text{A} + \text{B}(T/\text{K}) + \text{C}(T/\text{K})^2 + \text{D}(T/\text{K})^3$

	A	B	C	D
FA(g)[*]	3.3144×10^{1}	-1.1829×10^{-2}	6.6532×10^{-5}	-
FA(l)[**]	4.1631×10^{2}	-2.6391×10^{0}	4.9840×10^{-3}	-
W(g)[†]	1.9994×10^{2}	-1.5850×10^{0}	5.0964×10^{-3}	-5.5745×10^{-6}
W(l)[‡]	1.6123×10^{2}	-7.2947×10^{-1}	2.0340×10^{-3}	-1.8245×10^{-6}
Me(g)[†]	2.4977×10^{2}	-1.2274×10^{0}	1.9178×10^{-3}	-7.5224×10^{-7}
Me(l)[‡]	7.8123×10^{1}	-5.0381×10^{-2}	-2.2511×10^{-4}	1.4245×10^{-6}

Enthalpy of vaporization

	FA[¶]	W[s]	Me[§]
$\Delta_{\text{vap}} H^*_m$ (273.15 K)/(kJ·mol^{-1})	23.15	45.07	38.46

[*] From spectroscopic data cited by Walker (1964).

[**] From numbers determined using the estimation methods of Missenard (1965) and Rowlinson (1969) as recommended by Reid et al. (1987).

[†] Determined by Liu (1991) from a fit to data for the enthalpy of vaporization at different temperatures (Schmidt, 1982; Svoboda et al., 1973; Fiock et al., 1931) using the numbers for $\Delta_{\text{vap}} H^*_m$ (273.15 K) and $C^*_{p,m}$ (l) given in this table.

[‡] Taken from the compilation of Touloukian and Makita (1970).

[¶] From the vapor-pressure curve given by Maurer (1986).

[s] From the tables of Schmidt (1982).

[§] From experimental data of Svoboda et al. (1973) and Fiock et al. (1931) using the heat capacity correlations given in this table.

The partial molar excess enthalpy $H^E_m(i,T,\underline{x})$ is calculated using the UNIFAC method as discussed by Hasse and Maurer (1992).

In all equations given so far, true mole fractions are used and "molar" refers to the true mole number in the mixtures (chemical reactions taken into account). These true mole frac-

Table 2. Estimated Numbers for the Enthalpies of Vaporization and Reaction Enthalpies of Formaldehyde Reaction Products

Parameter	kJ·mol^{-1}	Sources	Method
$\Delta_{\text{vap}} H^*{}_m(MG, T)$	$\dfrac{16.605}{\left(1-\dfrac{142.72}{T/K}\right)^2}$	Maurer (1986)	*
	$\dfrac{33.261}{\left(1-\dfrac{57.72}{T/K}\right)^2}$ [§]	Hasse (1990)	*
$\Delta_{\text{vap}} H^*{}_m(HF, T)$	42.61	Maurer (1986)	*
	46.57[§]	Hasse (1990)	*
$\Delta_r H_m(MG, g, T)$	-61.95	Hall and Piret (1949)	**
	-43.12	Iliceto (1954)	**
	-43.51[§]	Kogan (1979a)	**
$\Delta_r H_m(HF, g, T)$	-49.31	Hall and Piret (1949)	**
	-53.73[§]	Kogan (1979a)	**
$\Delta_r H_m(MG_n, l, T)$	0.0	Koberstein et al. (1971)	†
	-2.76	Kogan (1979b)	†
	-0.234[§]	Hasse (1990)	‡
$\Delta_r H_m(HF_n, l, T)$	-7.00[§]	Kogan (1979b)	†
	3.62	Hasse (1990)	‡

[*] Determined from vapor-pressure curves estimated from vapor-liquid equilibrium data.

[**] Determined from gas density measurements.

[†] Determined from nuclear-magnetic resonance spectroscopic measurements.

[‡] Fitted to data of the heat of dilution.

[§] Used for prediction with the enthalpy model.

Table 3. Experimental Results for the Enthalpy Change upon Partial Vaporization of Aqueous Formaldehyde Solutions

T^{in}	T^{out}	m^g	m^l	$\tilde{x}_{FA}^{\text{in}}$	$\tilde{x}_{FA}^{\text{out}}$	$\tilde{y}_{FA}^{\text{out}}$	p_{exp}	Q_{el}		
K	K	g	g	——	mol·mol^{-1}	——	kPa	J	$\delta(\Delta p)$	$\delta(\Delta H)$
322.69	323.14	2.695	79.53	0.0000	0.0000	0.0000	12.35	6571.9	−0.08	−0.03
322.69	323.14	2.677	79.90	0.0000	0.0000	0.0000	12.32	6526.7	0.16	0.62
322.70	323.13	2.693	79.26	0.0000	0.0000	0.0000	12.31	6566.4	0.16	0.06
322.70	323.14	2.707	75.02	0.0000	0.0000	0.0000	12.33	6592.6	0.08	−0.37
322.70	323.19	2.719	88.02	0.1050	0.1098	0.0489	11.92	6607.0	−0.65	−2.21
322.70	323.17	2.722	81.95	0.1096	0.1125	0.0518	11.92	6565.2	−0.93	−2.00
322.70	323.14	2.753	81.32	0.1108	0.1129	0.0458	12.00	6622.3	−1.78	−1.58
322.70	323.14	2.763	82.82	0.1128	0.1149	0.0562	11.92	6600.2	−1.20	−1.44
322.70	323.15	2.736	83.15	0.1175	0.1203	0.0502	11.95	6567.4	−1.59	−1.54
322.71	323.14	2.747	69.25	0.1480	0.1528	0.0588	11.87	6567.7	−2.38	−2.08
322.70	323.15	2.750	89.15	0.1550	0.1571	0.0599	11.63	6569.3	−0.57	−1.51
322.70	323.19	2.694	85.18	0.1545	0.1592	0.0615	11.71	6568.9	−1.06	−3.44
322.68	323.21	2.693	83.87	0.1519	0.1608	0.0623	11.75	6569.5	−1.27	−3.38
322.71	323.18	2.743	85.13	0.1593	0.1617	0.0574	11.63	6568.8	−0.61	−1.60
322.70	323.19	2.708	85.68	0.1579	0.1623	0.0654	11.68	6568.9	−0.98	−3.19
322.69	323.15	2.696	85.02	0.1574	0.1624	0.0635	11.79	6570.7	−2.10	−3.70
322.70	323.19	2.699	85.04	0.1979	0.2044	0.0723	11.56	6569.6	−1.99	−3.99
322.71	323.16	2.786	82.73	0.2039	0.2086	0.0717	11.29	6567.8	−0.08	−1.13
322.71	323.13	2.799	83.16	0.2025	0.2092	0.0695	11.28	6624.3	−0.10	−1.52
322.70	323.16	2.742	89.32	0.2076	0.2153	0.0876	11.41	6565.9	−1.38	−3.30
342.71	343.14	2.729	77.42	0.0000	0.0000	0.0000	31.21	6514.8	−0.16	0.62
342.71	343.15	2.727	78.04	0.0000	0.0000	0.0000	31.17	6512.0	0.03	0.64
342.70	343.14	2.744	75.93	0.0000	0.0000	0.0000	31.21	6547.6	−0.16	0.04
342.70	343.15	2.741	74.56	0.0000	0.0000	0.0000	31.18	6506.0	0.00	0.11
342.71	343.13	2.766	76.61	0.0000	0.0000	0.0000	31.18	6593.4	0.10	−0.66
342.72	343.14	2.752	78.06	0.0000	0.0000	0.0000	31.20	6564.9	−0.13	−0.23
342.53	343.06	2.771	82.10	0.1273	0.1296	0.0873	30.98	6554.5	−1.44	−3.45
342.54	343.11	2.791	85.06	0.1286	0.1306	0.0878	30.93	6554.8	−1.07	−2.49
342.69	342.99	2.865	78.75	0.1446	0.1479	0.0977	30.66	6553.3	−1.15	−1.89
342.69	343.02	2.829	80.96	0.1459	0.1490	0.0876	30.66	6552.3	−1.05	−2.44
342.54	343.11	2.779	81.65	0.1511	0.1525	0.0953	30.65	6578.1	−0.75	−3.79
342.53	343.14	2.803	84.76	0.1691	0.1706	0.0919	30.66	6565.7	−1.15	−2.35
342.69	343.12	2.806	84.88	0.1754	0.1833	0.1108	30.33	6555.0	−0.43	−3.87
342.69	343.14	2.817	78.51	0.2088	0.2171	0.1112	30.10	6552.7	−0.64	−3.60
342.70	343.12	3.042	49.66	0.2100	0.2185	0.1102	30.10	6994.8	−0.85	−3.32
342.69	343.30	2.814	85.30	0.2559	0.2630	0.1398	29.56	6554.4	0.28	−4.26
362.67	363.15	5.028	83.35	0.0000	0.0000	0.0000	70.35	11639.1	−0.33	−0.21
362.67	363.12	5.042	74.44	0.0000	0.0000	0.0000	70.21	11660.6	−0.24	−0.12
362.67	363.13	5.003	74.89	0.0000	0.0000	0.0000	70.21	11574.3	−0.20	0.53
362.67	363.14	5.154	78.27	0.1056	0.1052	0.1009	71.97	11641.4	0.23	−2.67
362.66	363.15	5.176	79.82	0.1030	0.1000	0.0975	71.97	11632.8	0.23	−1.98
362.66	363.14	5.227	80.10	0.1639	0.1716	0.1419	71.98	11708.3	0.07	−3.76
362.66	363.23	5.275	81.01	0.2214	0.2293	0.1646	71.19	11637.7	0.81	−3.12
362.67	363.19	5.243	81.78	0.2104	0.2356	0.1767	71.39	11676.7	0.40	−4.62
362.68	363.15	5.235	79.02	0.2425	0.2505	0.1840	71.07	11631.9	0.30	−4.88
362.66	363.15	5.228	81.87	0.2477	0.2567	0.2021	71.09	11629.4	0.17	−5.65
362.67	363.15	5.328	84.41	0.2689	0.2750	0.1964	71.10	11632.8	−0.25	−3.70

tions are not a priori known but have to be calculated from (analytical) overall mole fractions and chemical equilibrium constants. In this work the set of chemical equilibrium constants given by Maurer (1986) was used. Vapor-pressure curves and activity coefficients are needed in this procedure to determine equilibrium constants for liquid phase reactions (methylene glycol and hemiformal formation) from the given numbers for the equilibrium constants of the same reactions in the gas phase. The vapor-pressure curves were taken from Hasse and Maurer (1991a), and the activity coefficients were calculated with the parameters given by Maurer (1986). The activity coefficients are also needed to determine the true liquid phase composition from the (thermodynamic) equilibrium constants. The algorithm used here is described in detail by Hasse (1990).

For enthalpy calculations numbers for the following properties are needed:

- Molar heat capacities of pure gaseous and liquid formaldehyde, water and methanol and the enthalpy of vaporization of these components at $T^{\theta} = 273.15$ K
- Enthalpies of vaporization of pure methylene glycol and hemiformal
- Reaction enthalpies for the formation of methylene glycol and hemiformal in the vapor phase

Table 4. Experimental Results for the Enthalpy Change upon Partial Vaporization of Methanolic Formaldehyde Solutions

T^{in}	T^{out}	m^g	m^l	$\tilde{x}_{FA}^{in}$	$\tilde{x}_W^{in}$	$\tilde{x}_{FA}^{out}$	$\tilde{x}_W^{out}$	$\tilde{y}_{FA}^{out}$	$\tilde{y}_W^{out}$	p_{exp}	Q_{el}		
K	K	g	g	mol·mmol^{-1}						kPa	J	$\delta(\Delta p)$	$\delta(\Delta H)$
311.84	313.12	4.026	47.40	0.3724	0.0336	0.3852	0.0387	0.1285	0.0346	15.89	4378.4	6.13	0.98
311.83	313.10	4.032	47.74	0.3792	0.0295	0.3854	0.0342	0.1281	0.0390	15.87	4381.1	5.74	1.32
312.19	313.17	4.215	47.90	0.3984	0.0306	0.4089	0.0330	0.1503	0.0357	15.05	4378.8	5.10	3.70
311.81	313.20	4.447	65.46	0.4029	0.0323	0.4175	0.0382	0.1569	0.0410	14.36	4749.9	7.28	2.14
312.20	313.33	4.382	61.84	0.4101	0.0333	0.4176	0.0335	0.1518	0.0364	14.76	4711.3	3.79	0.52
312.19	313.13	4.220	50.42	0.3902	0.0303	0.4197	0.0328	0.1550	0.0354	15.03	4380.0	4.14	3.49
312.19	313.16	7.283	108.23	0.4015	0.0313	0.4208	0.0321	0.1518	0.0364	14.76	7788.3	4.42	0.91
311.84	313.11	4.325	64.68	0.4068	0.0345	0.4241	0.0346	0.1520	0.0434	14.36	4679.2	4.97	0.84
311.68	313.14	4.175	50.80	0.4071	0.0320	0.4274	0.0341	0.1659	0.0398	14.01	4380.4	6.89	3.02
311.68	313.17	4.149	48.23	0.4060	0.0311	0.4433	0.0341	0.1744	0.0406	14.01	4380.3	4.39	1.89
311.84	313.08	4.372	77.24	0.5564	0.0388	0.5703	0.0394	0.2898	0.0969	6.83	4677.1	30.20	4.46
311.84	312.95	4.419	76.31	0.5479	0.0387	0.5733	0.0355	0.2843	0.0931	6.81	4687.9	31.24	4.56
332.11	333.19	4.082	47.12	0.3093	0.0255	0.3235	0.0277	0.1021	0.0215	49.54	4371.7	2.56	1.22
332.11	333.19	4.086	45.41	0.3084	0.0255	0.3235	0.0333	0.1041	0.0326	49.56	4371.0	2.27	1.98
332.11	333.18	4.147	46.34	0.3384	0.0241	0.3509	0.0287	0.1212	0.0253	45.54	4371.3	3.57	1.87
332.11	333.15	4.171	45.39	0.3409	0.0228	0.3535	0.0385	0.1216	0.0272	45.48	4371.8	2.22	2.41
331.38	333.18	4.087	48.73	0.3660	0.0258	0.3797	0.0298	0.1490	0.0357	40.36	4371.2	8.10	1.29
331.39	333.16	4.108	56.28	0.3592	0.0249	0.3910	0.0281	0.1504	0.0323	40.36	4369.7	7.88	1.93
331.38	333.18	4.453	60.34	0.4097	0.0321	0.4375	0.0321	0.1864	0.0426	34.66	4672.2	7.67	2.14
331.40	333.83	5.548	62.11	0.4184	0.0412	0.4426	0.0349	0.1927	0.0417	34.66	5945.6	6.79	0.10
331.39	333.14	4.167	52.16	0.5199	0.0402	0.5406	0.0382	0.3015	0.0866	20.64	4369.5	27.16	6.57
331.41	333.13	4.182	51.45	0.5269	0.0387	0.5456	0.0388	0.2985	0.0936	20.68	4370.3	24.34	7.28
331.38	333.14	4.285	70.04	0.5516	0.0400	0.5623	0.0370	0.3172	0.0860	19.61	4679.4	23.54	3.34
331.40	333.13	4.263	70.54	0.5498	0.0383	0.5628	0.0368	0.3118	0.0899	19.61	4674.0	23.89	3.03
332.07	333.16	4.139	51.79	0.5709	0.0370	0.5825	0.0353	0.3246	0.0890	18.57	4372.1	22.08	6.26
332.08	333.14	4.158	53.26	0.5617	0.0350	0.5827	0.0356	0.3249	0.0954	18.57	4378.7	24.15	7.38

- Reaction enthalpies for the formation of polyoxymethylene glycol and polyoxymethylene hemiformal in the liquid phase
- UNIFAC-parameters.

The pure component properties of formaldehyde, water and methanol are given in Table 1. For more detailed information on the determination of these parameters, see Hasse (1990) and Liu (1991). The reaction enthalpies as well as the enthalpies of vaporization of methylene glycol and hemiformal are more difficult to determine. As the formaldehyde reaction products do not exist as pure substances, these quantities cannot be determined directly, but have to be estimated from data on binary mixtures. Table 2 gives a survey of estimates for these quantities obtained from several sources.

The UNIFAC-parameters are needed to account for the change in the excess enthalpy of the liquid in the calorimeter. As only a very small amount of the liquid feed is evaporated, the enthalpy difference due to the excess enthalpy is also very small (typically less than 0.1% of the total enthalpy changes in the calorimeter for aqueous formaldehyde mixtures and less than 0.3% for methanolic mixtures). The UNIFAC parameter set of Hasse and Maurer (1992) was used in this work.

The enthalpy model can be extended in a straightforward manner to account for the presence of inert substances in formaldehyde-containing solutions. (A FORTRAN version of the model can be supplied by the authors.)

Experimental Results and Comparison with Predicted Enthalpy Changes

As changes of the potential and kinetic energy of the mass flow as well as the mechanical work transferred by rotating the coil can be neglected (Liu, 1991), the energy supplied by the electrical heater is equal to the enthalpy change of the mixture.

$$Q_{el} = \Delta H \tag{12}$$

The electric energy Q_{el} is determined experimentally, while the enthalpy change ΔH can be calculated with the enthalpy model using the experimental data for the temperature, composition and amount of mass of the vapor and liquid phases. The relative deviation $\delta(\Delta H)$ between the experimental electric energy Q_{el} and the calculated enthalpy change ΔH_{cal} is used to check the enthalpy model, while the relative deviation $\delta(\Delta p)$ between the experimental pressure p_{exp} and the pressure p_{cal} calculated using the vapor-liquid equilibrium model provides some (limited) information on whether the equilibrium is reached.

Tables 3 and 4 give experimental results for the partial vaporization for aqueous and methanolic formaldehyde mixtures respectively. Table 3 also contains some results of reference measurements on the partial vaporization of pure water. In both tables the experimental results are also compared with predictions (based on the pure component parameters given in Table 1 and the estimates of reaction enthalpies and enthalpies of vaporization of methylene glycol, hemiformal, polyoxymethylene glycol and polyoxymethylene hemiformal indicated in Table 2). In Figures 3 and 4, $\delta(\Delta H)$ values are plotted isothermally vs. the overall formaldehyde concentration $\tilde{x}_{FA}^{out}$ in the liquid phase leaving the calorimeter.

For aqueous formaldehyde-containing mixtures the exper-

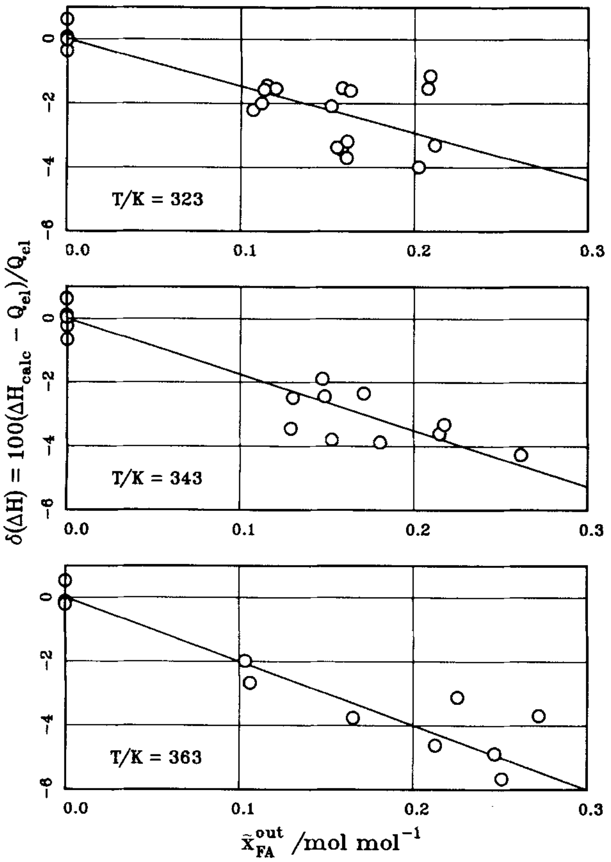

Figure 3. Predicted and measured enthalpy changes on partial vaporization of aqueous formaldehyde solutions.

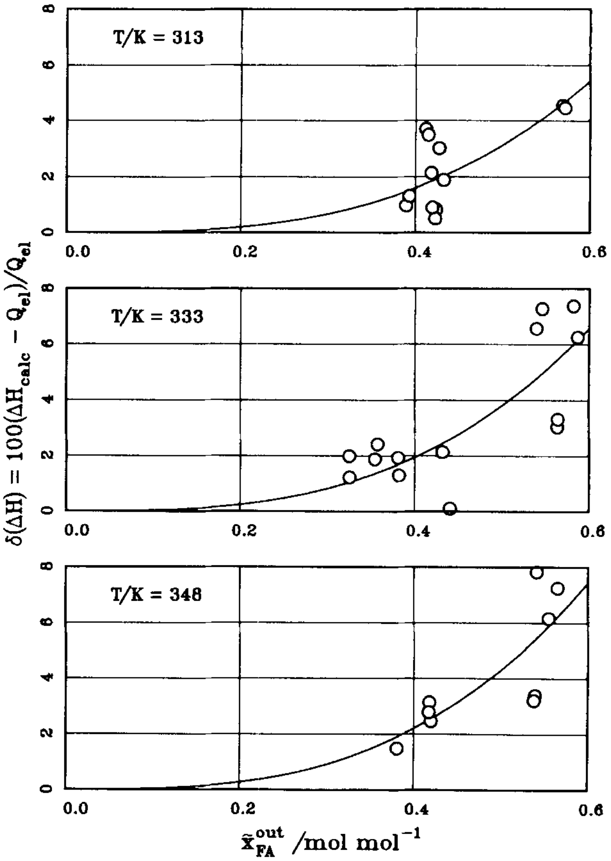

Figure 4. Predicted and measured enthalpy changes upon partial vaporization of methanolic formaldehyde solutions.

imental enthalpy changes are underestimated by the model, while for methanolic mixtures they are overestimated. A systematic increase in the relative deviation is observed as the formaldehyde concentration increases. The maximum deviations do not exceed 6% (aqueous formaldehyde solution with about 30 mol % formaldehyde) and 8% (methanolic formaldehyde solution with about 60 mol % formaldehyde) respectively. For methanolic mixtures, large $\delta(\Delta H)$ values occur together with relative large concentrations of water in the liquid phase (about 4 mol %). Generally, temperature has only a small influence on the deviations. In aqueous formaldehyde mixtures calculated and measured total pressures agree within about 1%. In methanolic formaldehyde mixtures at overall formaldehyde concentration of less than about 40 mol % the calculated total pressures agree with the experimental results within about 5%. At high formaldehyde concentration deviations are considerably larger. In that range the vapor-liquid equilibrium model had not been tested before due to the lack of experimental data. These large positive deviations can, however, also be an indication, that the equilibrium was not completely reached in the experiments (it is known, that the chemical reactions in methanolic formaldehyde solutions are considerably slower than those in aqueous solutions).

Improvements

Improvements were achieved by fitting some of those parameters, which cannot be determined directly (cf. Table 2), to the new experimental results. The vapor-liquid equilibrium model remains unchanged even though parameters of both models are interrelated as, for example, enthalpy of vaporization and vapor-pressure or reaction enthalpy and chemical reaction constant. The parameters given in Table 1 and the UNIFAC-parameters remain unchanged.

For the formaldehyde + water system, a sensitivity analysis showed that only the numbers for the reaction enthalpy of the methylene glycol formation in the vapor phase and the enthalpy of vaporization of methylene glycol have an essential influence on the predicted enthalpy changes upon partial vaporization, while the influence of the other parameters given in Table 2 can be neglected. It is sufficient to fit one of the sensitive parameters to obtain a considerably improved correlation. The reaction enthalpy of the methylene glycol formation was chosen for this purpose.

Table 5 gives new numbers for the reaction enthalpy of the methylene glycol formation. They are within the scattering of the estimates given in Table 2. By using the new numbers obtained from isothermal fits the systematic deviations shown in Figure 3 are completely removed and deviations between calculated and measured enthalpy changes are generally reduced to ±1% (see Figure 5). Using the temperature independent reaction enthalpy, also given in Table 5, results in a somewhat poorer agreement but deviations are still within ±2%.

Table 5. Numbers for the Reaction Enthalpy of the Methylene Glycol Formation in the Gas Phase (Fitted to the Experimental Data of This Work)

Parameter	Temperature Dependence	T/K 323	343	363	Method
$\Delta_r H_m(MG, g, T)$/ kJ·mol^{-1}	yes	−63.10	−58.66	−54.99	I
	no		−56.38		II

Table 6. Comparison between the Heat of Solution of Formaldehyde Gas in Water $\Delta_{sol}H_m$/kJ·mol^{-1} at 294 K as reported by Walker (1933) and Calculated with the Enthalpy Model

	Walker Exp.	Calculation Method* I	II**
$\Delta_{sol}H_m$/kJ·mol^{-1}	−62.0	−63.7	−76.2

*Compare with Table 5.
**$\Delta_r H_m$ (MG, g, 294 K)/kJ·mol^{-1} = −68.9.

If instead of the reaction enthalpy, the enthalpy of vaporization of methylene glycol is fitted to the data, the new numbers are distinctly greater than the estimates from the vapor-pressure curves. Therefore the enthalpy of vaporization of methylene glycol was kept unchanged.

Walker (1933) and Delépine (1897) report experimental results for the heat of solution of formaldehyde gas in water at room temperature, which is below the temperature range investigated in the present work. Both authors give a concentration independent value of about −62 kJ mol^{-1}. For the conditions of Walker's experiment a comparison between the experimental result and the calculations with the enthalpy model is given in Table 6. Using the temperature independent number for the reaction enthalpy of the methylene glycol formation fitted in this work yields a satisfactory agreement, while predictions based on the temperature dependence of the reaction enthalpy (cf. Table 5; assuming a linear relation between this parameter and temperature) show relative deviations of about 20%. This is not surprising as assuming that linear relation between $\Delta_r H_m$ and the temperature overestimates the influence of temperature on $\Delta_r H_m$.

For the formaldehyde + methanol + water system, a detailed analysis showed, that the number for the enthalpy of vaporization of hemiformal $\Delta_{vap}H_m^*(HF,T)$ has the largest influence on the prediction. The number for the reaction enthalpy of the hemiformal formation in the vapor phase $\Delta_r H_m(HF,g,T)$ is less, but still important. Contrarily to the formaldehyde + water system, where the polymer-formation has virtually no influence on the calculation of enthalpy changes upon

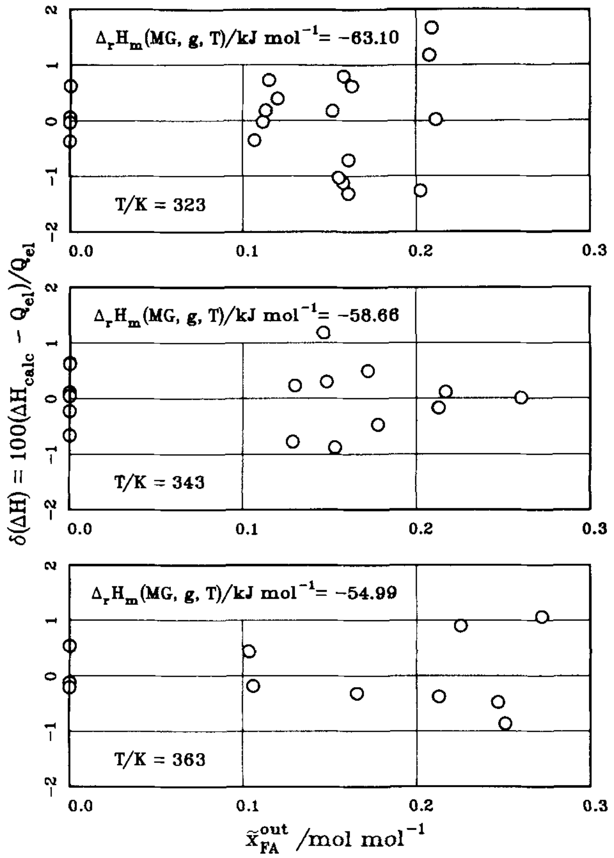

Figure 5. Calculated and measured enthalpy changes upon partial vaporization of aqueous formaldehyde solutions.

Calculated using method I of Table 5.

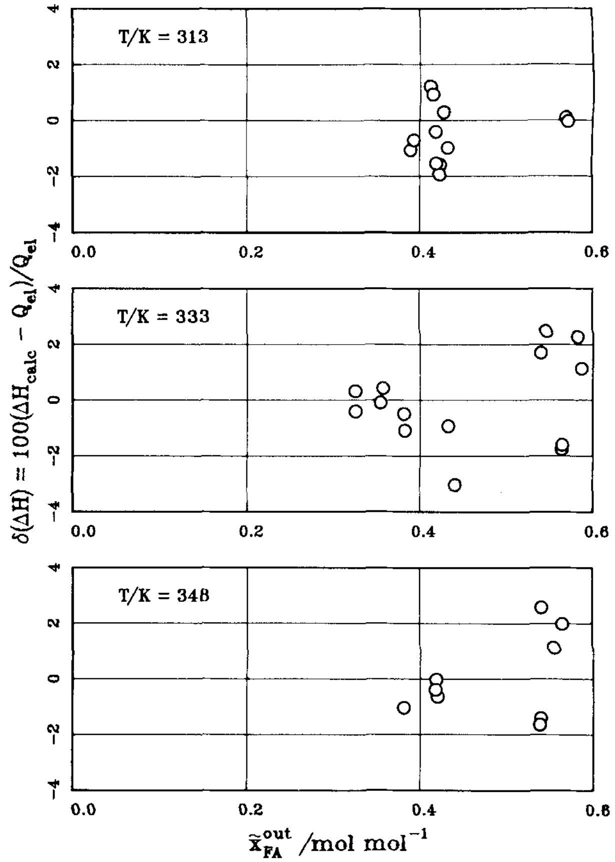

Figure 6. Calculated and measured enthalpy changes upon partial vaporization of methanolic formaldehyde solutions.

Calculated using method II of Table 7.

Table 7. Numbers for the Enthalpy of Vaporization of Hemiformal (Fitted to the Experimental Data of This Work)

Parameter	Temperature Dependence	T/K 313	 333	 348	Method
$\Delta_{vap}H^*_m(\mathrm{HF},T)$/ kJ·mol^{-1}	yes	42.01	41.12	40.92	I
	no		41.26		II

partial vaporization, the polyoxymethylene hemiformal formation $\Delta_r H_m(HF_n,l,T)$ has a small but nonnegligible influence.

By separately fitting $\Delta_{vap}H^*_m(HF)$, $\Delta_r H_m(HF,g)$ or $\Delta_r H_m(HF_n, l)$, predictions can be improved considerably, even when these quantities are considered to be temperature independent. However, only the resulting parameter for $\Delta_{vap}H^*_m(HF)$ is within the range of the estimates from the various sources given in Table 2. With the new number for $\Delta_{vap}H^*_m(HF)$ (cf. Table 7) the systematic deviation between experimental data and calculation is completely removed, the relative deviations are now generally within ±2% (cf. Figure 6). Allowing for an influence of temperature on $\Delta_{vap}H^*_m(HF)$ results only in a minor improvement. This is not surprising as the influence of temperature on $\Delta_{vap}H^*_m(HF)$ is rather small (cf. Table 7).

Walker (1933) also measured the heat of solution of formaldehyde gas in methanol at around room temperature. The results are virtually identical with those obtained by the same author for the solution of formaldehyde in water. Model predictions of heats of solution of formaldehyde gas in methanol are compared to Walker's data in Table 8. The relative deviation is about 8%. As could be expected, the results obtained using temperature dependent or independent numbers for $\Delta_{vap}H^*_m(HF)$ differ only slightly.

Conclusions

Aqueous and methanolic formaldehyde mixtures are examples of complex systems in which chemical reactions and intermolecular forces have an essential influence on thermodynamic properties. The physicochemical vapor-liquid equilibrium model of Maurer (1986) is extended in this work to calculate enthalpy differences upon vaporization of aqueous and methanolic formaldehyde mixtures. In an especially designed flow calorimeter, aqueous and methanolic formaldehyde-containing mixtures with formaldehyde concentrations of up to 0.3 mol/mol (formaldehyde + water) and 0.6 mol/mol (formaldehyde + methanol) were partially vaporized without taking the risk of polymer precipitation. Comparisons between the new experimental data and model predictions show deviations of a only few percent, even though several important model parameters had to be estimated from noncalorimetric measurements. By fitting some formerly estimated parameters to the calorimetric data of this work the deviations are reduced to ±1% for aqueous solutions and ±2% for methanolic solutions. The new parameters are within the scattering of estimates from noncalorimetric sources.

Table 8. Comparison between the Heat of Solution of Formaldehyde Gas in Methanol $\Delta_{sol}H_m$/kJ·mol^{-1} at 296 K as Reported by Walker (1933) and Calculated with the Enthalpy Model

	Walker Exp.	Calculation Method* I**
$\Delta_{sol}H_m$/kJ·mol^{-1}	−62.8	−58.2

*Compare with Table 7.
**$\Delta_{vap}H^*_m$ (HF, 296 K)/kJ·mol^{-1} = 42.4.

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Notation

C_p = heat capacity at constant pressure
FA = formaldehyde
g = gas
H = enthalpy
H^E = excess enthalpy
HF = hemiformal
HF_n = polyoxymethylene hemiformal (n = number of CH_2O groups)
i = component
l = liquid
m = amount of mass of sample
Me = methanol
MG = methylene glycol
MG_n = polyoxymethylene glycol (n = number of CH_2O groups)
p = pressure
Q_{el} = electric energy
T = temperature
W = water
x = true liquid-phase mole fraction
$\tilde{x}$ = overall liquid-phase mole fraction
$\underline{x}$ = vector describing the true liquid-phase composition
y = true gas-phase mole fraction
$\tilde{y}$ = overall gas-phase mole fraction
$\underline{y}$ = vector describing the true gas-phase composition
ΔH = enthalpy change
$\Delta_r H$ = reaction enthalpy
$\Delta_{sol}H$ = heat of solution
$\Delta_{vap}H$ = enthalpy of vaporization
$\delta(\Delta H)$ = $100\,(\Delta H_{calc} - Q_{el})/Q_{el}$
$\delta(\Delta p)$ = $100\,(p_{calc} - p_{exp})/p_{exp}$

Subscripts

calc = calculated
exp = experimental
FA = formaldehyde
m = molar or partial molar
W = water

Superscripts

g = gas phase
in = calorimeter inlet
l = liquid phase
out = calorimeter outlet
$*$ = pure component
θ = standard state

Literature Cited

Delépine, M., "Chaleurs de Formation de l'Aldéhyde Formique, Dissous et Gaseux," *Compt. Rend. Acad. Sci. Paris*, **124**, 816 (1897).

Fiock, E. F., D. C. Ginnings, and W. B. Holton, "Calorimetric Determination of Thermal Properties of Methyl Alcohol, Ethyl Alcohol and Benzene," *Bur. Stand. J. Res.*, **6**, 881 (1931).

Gmehling, J., P. Rasmussen, and A. Fredenslund, "Vapor-Liquid

Equilibria by UNIFAC Group Contribution. Revision and Extension 2," *Ind. Eng. Chem. Proc. Des. Dev.*, **21**, 118 (1982).

Hall, M. W., and P. T. Piret, "Distillation Principles of Formaldehyde Solutions," *Ind. Eng. Chem.*, **41**, 1277 (1949).

Hasse, H., "Dampf-Flüssigkeits-Gleichgewichte, Enthalpien und Reaktionskinetik in formaldehydhaltigen Mischungen," PhD Thesis, Universität Kaiserslautern (1990).

Hasse, H., I. Hahnenstein, and G. Maurer, "Revised Vapor-Liquid Equilibrium Model for Multicomponent Formaldehyde Mixtures," *AIChE J.*, **36**, 1807 (1990).

Hasse, H., and G. Maurer, "Vapor-Liquid Equilibrium of Formaldehyde-Containing Mixtures at Temperatures below 320 K," *Fluid Phase Equilibria*, **64**, 185 (1991a).

Hasse, H., and G. Maurer, "Kinetics of the Poly(oxymethylene) Glycol Formation in Aqueous Formaldehyde Solutions," *I&EC Research*, **30**, 2195 (1991b).

Hasse, H., and G. Maurer, "Heat of Dilution in Aqueous and Methanolic Formaldehyde Solutions," *Ber. Buns. Ges. Phys. Chem.*, **96**, 1, 83 (1992).

Iliceto, A., "Sul sistema acqua-formaldeide. Nota IV. Equilibri delle fasi liquida e gassosa," *Gazz. Chim. Ital.*, **84**, 536 (1954).

Koberstein, E., K. P. Müller, and G. Nonnenmacher, "Molekulargewichtsverteilung von Formaldehyde in wäßrigen Lösungen," *Ber. Buns. Ges. Phys. Chem.*, **75**, 549 (1971).

Kogan, L. V., "State of the Vapor Phase above Solutions of Formaldehyde in Water and Methanol," *Zhur. Prikl. Khim.*, **52**, 2722 (1979a).

Kogan, L. V., "NMR-Study of the State of Aqueous Methanol Solutions of Formaldehyde," *Zhur. Prikl. Khim.*, **52**, 2725 (1979b).

Liu, Y.-Q., "Enthalpieänderungen beim Verdampfen wäßriger und methanolischer Formaldehydlösungen," PhD Thesis, Universität Kaiserslautern (1991).

Liu, Y.-Q., and G. Maurer, "Flow-Calorimeter for Measuring Enthalpy Changes during the Partial Vaporization of Mixtures," *J. Chem. Thermodynamics*, **24**, 1109 (1992).

Majer, V., V. Svoboda, and J. Pick, "Heats of Vaporization of Fluids," Studies in Modern Thermodynamics 9, Elsevier, Amsterdam (1989).

Maurer, G., "Vapor-Liquid Equilibrium of Formaldehyde- and Water-Containing Multicomponent Mixtures," *AIChE J.*, **32**, 932 (1986).

Missenard, F. A., "Méthode Additive pour la Détermination de la Chaleur Molaire des Liquides," *Compt. Rend. Acad. Sci. Paris* **260**(5), 5521 (1965).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw Hill, New York (1987).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, 2nd ed., Butterworth, London (1969).

Schmidt, E., *Properties of Water and Steam in SI Units 0–800°C, 0–1000 bar*, 3rd enl. pr., Springer, Berlin (1982).

Svoboda, V., F. Vesely, R. Holub, and J. Pick, "Enthalpy Data of Liquids. II. The Dependence of Heats of Vaporization of Methanol, Propanol, Butanol, Cyclohexane and Benzene on Temperature," *Coll. Czechoslov. Chem. Comm.*, **38**, 3539 (1973).

Touloukian, Y. S., and T. Makita, *Specific Heat Nonmetallic Liquids and Gases, Thermophysical Properties of Matter*, Vol. 6, IFI Plenum, New York (1970).

Ullmann's Encyclopedia of Industrial Chemistry, Vol. A, Alphabetically Arranged Articles, Vol. 11, Fibers, Synthetic Inorganic to Formaldehyde, 5th comp. rev. ed., VCH Weinheim (1988).

Walker, J. F., "Some Properties of Anhydrous Formaldehyde," *J. Am. Chem. Soc.*, **55**, 2821 (1933).

Walker, J. F., *Formaldehyde*, ACS Monograph, 3rd ed., Reinhold, New York (1964).

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