Thermodynamics of the HSO_4^- Formation in Aqueous Solutions up to 473 K and 975 bar

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The equilibrium constant, partial molal volume, entropy and enthalpy of the formation of HSO_4^- ion in aqueous solutions have been determined up to 473 K and 975 bar at the ionic strengths $I=0$ as well as in NaCl solutions having $I = 1$, 0.5 and 0.1 mol kg^{-1}. At 473 K, for instance, the thermodynamic formation constant K^0 decreases by ≈ 0.75 log units from saturation pressure to 975 bar. The corresponding decrease of the apparent formation constant Q at $I=1$ m is ≈ 0.6 log units. The increased dissociation at higher pressure leads to a decrease of the partial molal volume and entropy due to the resulting higher electrostriction in the system.

1. Introduction

Knowledge of the formation constant of HSO_4^- in aqueous solutions under high temperature and pressure is necessary for the thermodynamic characterization of various technical and geochemical hydrothermal systems containing SO_4^{2-}. Various authors [1–9] have determined this constant up to 623 K along with the corresponding saturation pressure. Studies under higher pressures are lacking, probably because the pressure effect on the equilibrium constant of ion association in aqueous solutions is, in general, thought to be much smaller than the temperature effect.

However, with respect to the solar energy storage, potential assisted photoelectrolysis of SO_4^{2-} containing water at high temperatures and pressures is presently investigated in our institute. Current/voltage curves obtained from cyclic voltammetric measurements using an $Ag-Ag_2SO_4$ electrode as a reference, are analysed to study this process. Knowledge of the formation constant of HSO_4^- is necessary for the calculation of the potential of the $Ag-Ag_2SO_4$ electrode, as well as for the interpretation of such curves.

We have, therefore, determined the apparent formation constant (Q) of HSO_4^- up to 473 K and 975 bar by means of potentiometric measurements in aqueous NaCl media having the ionic strengths $I = 1$, 0.5 and 0.1 m, using the high temperature – high pressure cell described by Becker and Bilal [10]. The thermodynamic formation constant (K^0) was then determined by extrapolation to $I=0$ of the equation

$$\log K^0 = \log Q + 4 A\gamma I^{1/2}/(1 + B\gamma \mathring{a} I^{1/2}) . \quad (1)$$

The Debye-Hückel term (second term on the r.h.s. of (1)) was first calculated from the values of $\log K^0$ and $\log Q$ (in NaCl media of $I=0.1-5$ m) determined by Dickson, Wesolowski, Palmer, and Mesmer [9] at different temperatures along with the corresponding saturation pressures. To obtain its value at higher pressures, the coefficients $A\gamma$ and $B\gamma$ were corrected to their values at the pressure of interest given by Helgeson and Kirkham [11]. The values corresponding to pressures not explicitly given there were interpolated from plots of $(A\gamma)_T$, respectively $(B\gamma)_T$ as functions of pressure. Log $Q(I)$, obtained at every constant temperature and pressure was then plotted vs. $I^{1/2}(1 + B\gamma \mathring{a} I^{1/2})$, and $\log K^0$ was determined at $I=0$. Practically no deviation from linearity was observed in these plots, which means that the right values of the Debye-Hückel term were used.

2. Experimental

The following electrochemical cell was used for the measurement (all concentrations are in molal units mol kg^{-1}):

	Sample (s)	Intermediate electrolyte	Reference (r)	
Pt–H_2	$x = 0.025$ m HCl $y = 0.01$ m Na_2SO_4 $z = (I-x-3y)$ m NaCl	I m NaCl	0.001 m HCl $I-0.001$ m NaCl	H_2–Pt, (2)

where $I=1$, 0.5 and 0.1 m.

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The air in the autoclave was replaced by repeated pressurizing with pure hydrogen (99.999%) to 31 bar at 298 K. Further initial pressures at 298 K were obtained by pressurizing of purified Ar to 82, 130, 185, 236, 287, 336, 382, 485, and 590 bar. These pressures increased with the temperature to 60, 146, 231, 326, 428, 528, 632, 732, 863, and 975 bar et 473 K, respectively.

The potential difference between the sample and reference compartments is given by

$$\Delta E = -(RT/F)\ln([H^+]_s/[H^+]_r) - (RT/F)\ln[(\gamma_{H^+})_s/(\gamma_{H^+})_r] + E_{lj}\,. \quad (3)$$

The magnitude of the liquid junction potential was estimated from the Henderson equation to be ≤ 0.5 mV. The stoichiometric activity coefficients of the hydrogen ion in both compartments could be assumed to be the same in the presence of a swamping electrolyte, so that the second term on the right hand side of (3) reduces to zero.

3. Results and Discussion

The apparent formation constant of the reaction

$$H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-,$$

$$Q = [HSO_4^-]/[H^+]\,[SO_4^{2-}] \quad (4)$$

is calculated using $[H^+]$ obtained from (3),

$$[HSO_4^-] = x - [H^+] \quad (5)$$

and

$$[SO_4^{2-}] = y - x + [H^+] - [NaSO_4^-] = (y - x + [H^+])/(1 + \delta\,[Na^+])\,, \quad (6)$$

where

$$[Na^+] = C_{Na^+}/(1 + \delta\,[SO_4^{2-}])\,. \quad (7)$$

C_{Na^+} denotes the total concentration of $Na = 2y + z$ and δ is the apparent formation constant of $NaSO_4^-$. Its values as functions of I, T, and p were calculated from $\log K^0_{NaSO_4^-}$ given by Oscarson, Izatt, Brown, Pawlak, Gillespie and Christensen [8] at the different temperatures and the corresponding saturation pressure and the Debye-Hückel term, using the ion-size parameter $\mathring{a}_{NaSO_4^-}$ given by Helgeson, Kirkham and Flowers [12] as well as the coefficients $A\gamma(T, p)$ and $B\gamma(T, p)$ reported in [11]. From (4), (5), (6), and (7)

$$Q = (x - [H^+])\,(1 + \delta\,[Na^+])/(y - x + [H^+])\,[H^+]\,, \quad (8)$$

where $[Na^+]$ is determined iteratively by fitting (6) and (7), taking $[SO_4^{2-}] = y - x[H^+]$ for the first iteration step.

Table 1 contains the Debye-Hückel term, $\log Q(I)$ and $\log K^0$ at the different temperatures and pressures. The values at saturation pressures are taken from [9]. Figure 1 shows $\log K^0$, and (as an example) $(\log Q)_{1.0\,m}$ as function of the pressure at different constant temperatures. The extention of these graphs down to the corresponding saturation pressures yields almost the same values given in [9].

The partial molal volume of reaction (4) at $I = 0$, $(\Delta\bar{V}^0)$, as well as at $I = 1$ m, $(\Delta\bar{V})_{1.0\,m}$, were determined from the slopes of the curves in Fig. 1 at various pressure values according to

$$-2.303\,RT\,(\partial \log K^0/\partial p)_T = \Delta\bar{V}^0(p)\,, \quad (9)$$

$$-2.303\,RT\,(\partial \log Q(I)/\partial p)_T = \Delta\bar{V}(I, p)\,, \quad (10)$$

and are summarized in Table 2.

The pressure dependence of $\log K^0$ and $\log Q(I)$ at constant T is given by the integral of (9) and (10) from 1 bar (saturation pressure up to 373 K) to the higher pressure p. An expression of the form

$$-\log[(K^0)^p/(K^0)^1] = [\Delta\bar{V}^{01}/2.303\,RT]\,f(p)\,, \quad (11)$$

$$-\log[Q(I)^p/Q(I)^1] = [\Delta\bar{V}(I)^1/2.303\,RT]\,f(p) \quad (12)$$

is next used to account for the pressure dependence of $\Delta\bar{V}^0$ and $\Delta\bar{V}(I)$ accompanying the formation of weak acids and bases in water, where $f(p)$ is a function of pressure which would be equal to p if $\Delta\bar{V}^0$ and $\Delta\bar{V}(I)$ were independent of pressure. Owen and Brinkley [13] proposed a logarithmic form for $f(p)$, which works rather well but requires two adjustable parameters in addition of $\Delta\bar{V}^{01}$, respectively $\Delta\bar{V}(I)^1$. El'yanov and Gonikberg [14] later found that $f(p)$ is actually a universal function for the ionisation of a wide range of weak acids and bases in water, which is virtually independent of the temperature and the reaction system. El'yanov and Hamann [15] subsequently showed that it could be expressed analytically by

$$f(p) = p/(1 + b\,p)\,, \quad (13)$$

where for aqueous solutions b is a constant $= 9.2 \times 10^{-5}$ bar^{-1}.

To check the validity of this expression for (11) and (12) as well as for the integration of (9) and (10) from the saturation pressures to higher ones at $T > 373$ K, $\log k^0$ and $\log (Q)_{1.0\,m}$ were plotted at the different

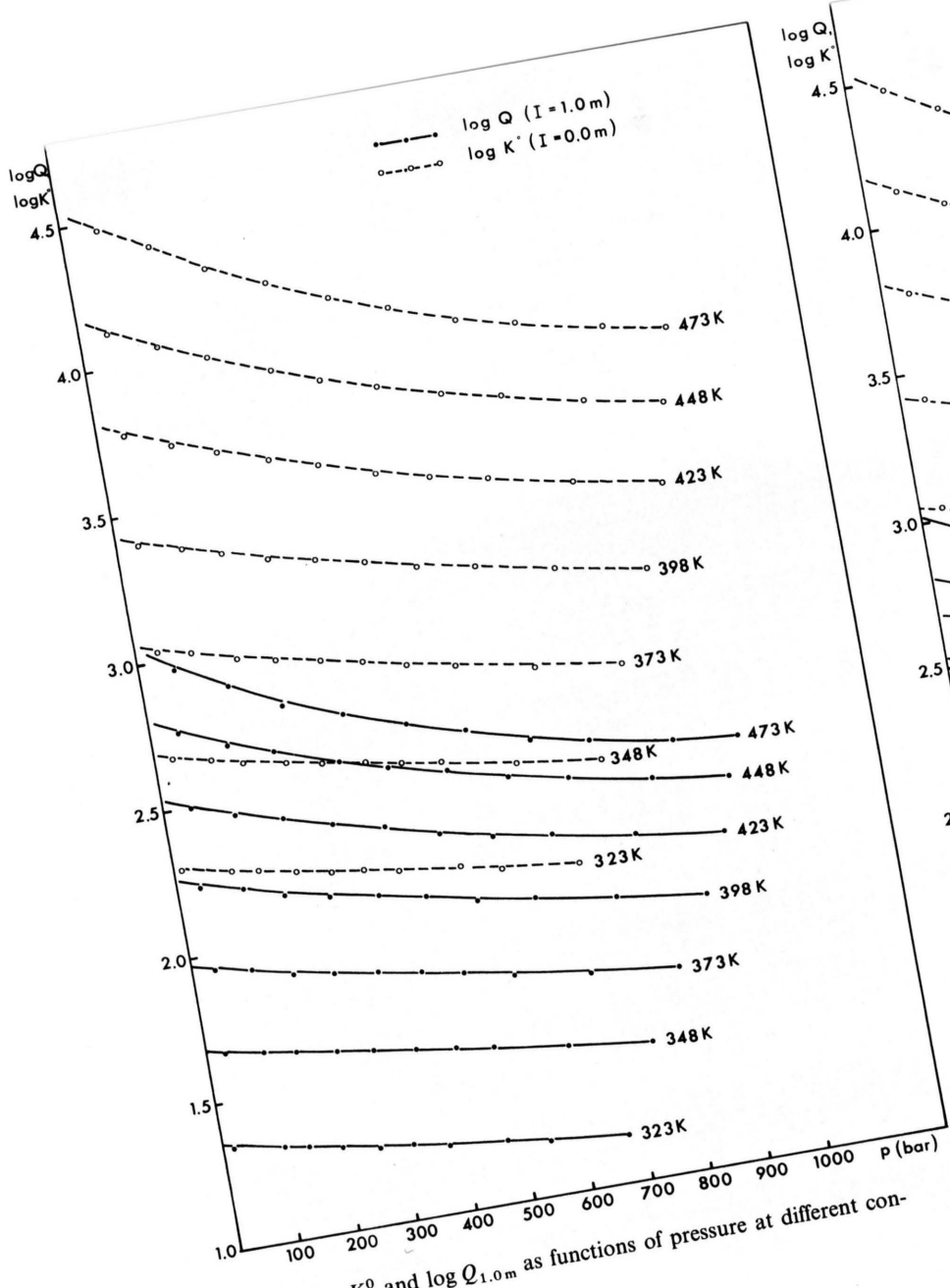

Fig 1. $\log K^0$ and $\log Q_{1.0\,m}$ as functions of pressure at different constant temperatures.

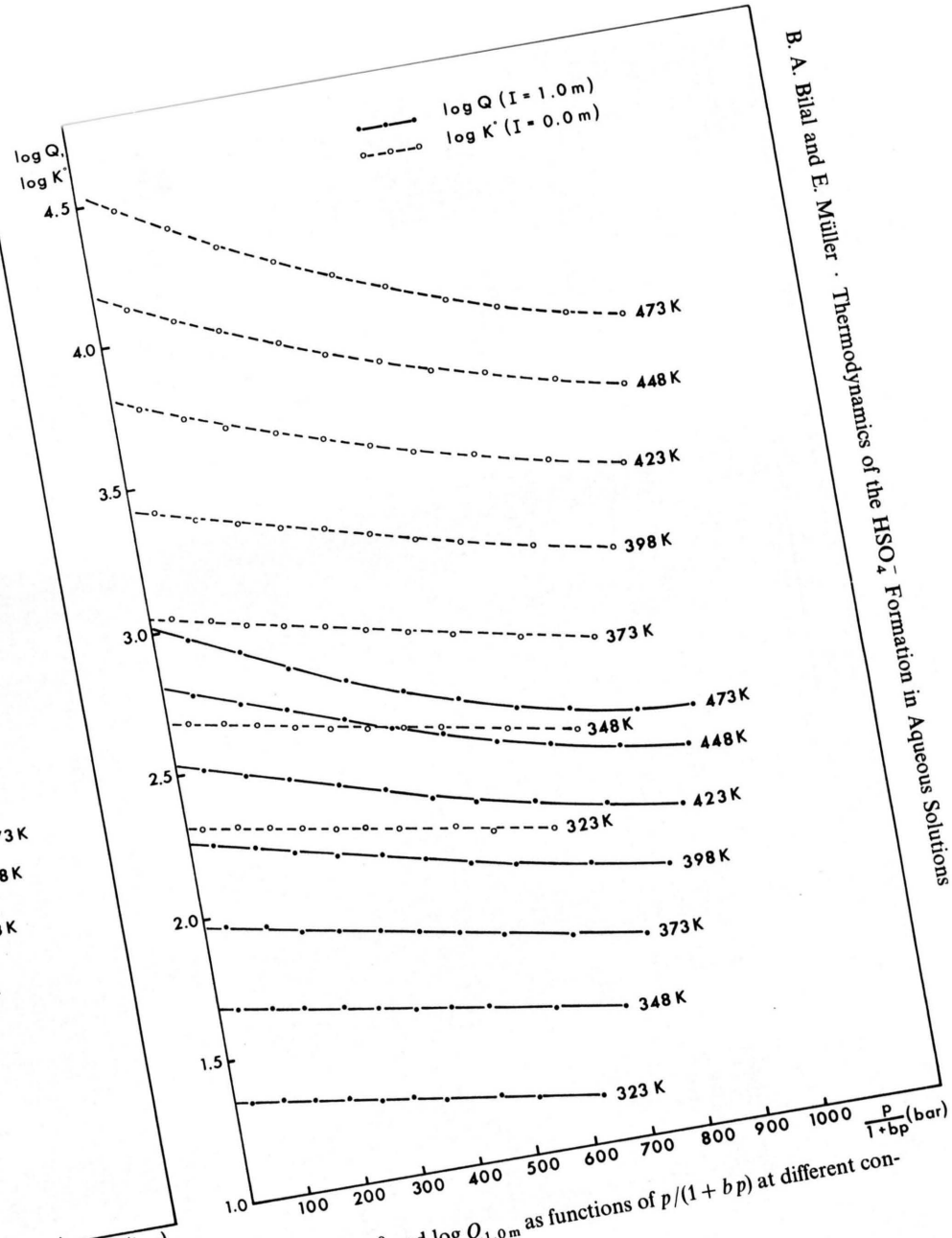

Fig. 2. $\log K^0$ and $\log Q_{1.0\,m}$ as functions of $p/(1 + b\,p)$ at different constant temperatures.

Table 1. Debye-Hückel term (DHT), log Q and log K^0 at different I, T, and p. The values at saturation pressure (sat.) are taken from [9].

p (bar)	$I = 1.0$ m		$I = 0.5$ m		$I = 0.1$ m		log K^0
	DHT	log Q	DHT	log Q	DHT	log Q	
				323 K			
sat.	0.958	1.358 ± 0.010	0.823	1.493 ± 0.009	0.499	1.817 ± 0.010	2.316 ± 0.012
33	0.957	1.346 ± 0.012	0.816	1.487 ± 0.010	0.495	1.808 ± 0.009	2.303 ± 0.011
88	0.954	1.330 ± 0.009	0.814	1.470 ± 0.011	0.493	1.791 ± 0.010	2.284 ± 0.010
141	0.951	1.314 ± 0.010	0.812	1.453 ± 0.009	0.492	1.773 ± 0.011	2.265 ± 0.011
201	0.949	1.296 ± 0.011	0.810	1.435 ± 0.010	0.491	1.754 ± 0.012	2.245 ± 0.012
260	0.948	1.277 ± 0.009	0.808	1.417 ± 0.009	0.490	1.735 ± 0.010	2.225 ± 0.010
316	0.946	1.261 ± 0.010	0.807	1.400 ± 0.011	0.489	1.718 ± 0.009	2.207 ± 0.011
375	0.945	1.244 ± 0.011	0.806	1.383 ± 0.010	0.488	1.701 ± 0.011	2.189 ± 0.009
475	0.943	1.213 ± 0.009	0.803	1.353 ± 0.009	0.487	1.669 ± 0.010	2.156 ± 0.012
546	0.940	1.194 ± 0.010	0.801	1.333 ± 0.011	0.486	1.648 ± 0.009	2.134 ± 0.009
670	0.935	1.169 ± 0.011	0.797	1.307 ± 0.010	0.483	1.621 ± 0.011	2.104 ± 0.010
				348 K			
sat.	1.017	1.669 ± 0.005	0.869	1.817 ± 0.005	0.525	2.161 ± 0.007	2.686 ± 0.009
36	0.996	1.665 ± 0.004	0.865	1.796 ± 0.006	0.522	2.139 ± 0.005	2.661 ± 0.007
95	0.991	1.655 ± 0.006	0.860	1.786 ± 0.004	0.520	2.126 ± 0.006	2.646 ± 0.008
153	0.988	1.634 ± 0.005	0.858	1.764 ± 0.005	0.518	2.104 ± 0.007	2.622 ± 0.010
219	0.986	1.611 ± 0.004	0.856	1.741 ± 0.007	0.517	2.080 ± 0.008	2.597 ± 0.009
283	0.982	1.590 ± 0.006	0.848	1.724 ± 0.004	0.515	2.057 ± 0.005	2.572 ± 0.007
347	0.980	1.570 ± 0.005	0.846	1.704 ± 0.006	0.514	2.036 ± 0.007	2.550 ± 0.008
414	0.977	1.551 ± 0.004	0.844	1.684 ± 0.005	0.512	2.016 ± 0.006	2.528 ± 0.009
483	0.975	1.530 ± 0.005	0.842	1.663 ± 0.006	0.511	1.994 ± 0.008	2.505 ± 0.009
606	0.969	1.496 ± 0.006	0.836	1.629 ± 0.007	0.508	1.957 ± 0.007	2.465 ± 0.008
741	0.962	1.461 ± 0.005	0.830	1.593 ± 0.006	0.504	1.919 ± 0.008	2.423 ± 0.009
				373 K			
sat.	1.089	1.972 ± 0.004	0.926	2.135 ± 0.004	0.557	2.504 ± 0.006	3.061 ± 0.008
39	1.082	1.959 ± 0.006	0.920	2.121 ± 0.005	0.554	2.487 ± 0.005	3.041 ± 0.009
103	1.075	1.933 ± 0.005	0.914	2.094 ± 0.004	0.550	2.458 ± 0.006	3.008 ± 0.008
167	1.072	1.906 ± 0.006	0.911	2.067 ± 0.005	0.548	2.434 ± 0.005	2.978 ± 0.007
237	1.068	1.878 ± 0.004	0.908	2.037 ± 0.006	0.546	2.400 ± 0.005	2.946 ± 0.008
308	1.065	1.851 ± 0.005	0.906	2.010 ± 0.004	0.544	2.371 ± 0.006	2.916 ± 0.007
378	1.062	1.824 ± 0.006	0.903	1.983 ± 0.005	0.543	2.343 ± 0.006	2.886 ± 0.009
453	1.058	1.798 ± 0.004	0.900	1.956 ± 0.005	0.541	2.315 ± 0.005	2.856 ± 0.008
534	1.055	1.771 ± 0.005	0.897	1.929 ± 0.006	0.539	2.287 ± 0.006	2.826 ± 0.009
664	1.046	1.734 ± 0.006	0.889	1.891 ± 0.006	0.535	2.304 ± 0.006	2.780 ± 0.009
809	1.038	1.696 ± 0.006	0.882	1.852 ± 0.006	0.530	2.204 ± 0.007	2.734 ± 0.010
				398 K			
sat.	1.175	2.261 ± 0.003	0.994	2.442 ± 0.003	0.596	2.840 ± 0.005	3.436 ± 0.007
43	1.163	2.246 ± 0.004	0.984	2.425 ± 0.005	0.590	2.819 ± 0.006	3.409 ± 0.008
111	1.158	2.209 ± 0.005	0.980	2.387 ± 0.004	0.587	2.780 ± 0.005	3.367 ± 0.007
181	1.153	2.174 ± 0.004	0.975	2.351 ± 0.004	0.585	2.742 ± 0.005	3.327 ± 0.008
256	1.148	2.138 ± 0.004	0.971	2.315 ± 0.005	0.582	2.704 ± 0.006	3.286 ± 0.008
335	1.143	2.103 ± 0.005	0.967	2.279 ± 0.004	0.579	2.667 ± 0.006	3.246 ± 0.009
412	1.137	2.073 ± 0.005	0.962	2.248 ± 0.006	0.577	2.633 ± 0.007	3.210 ± 0.009
495	1.132	2.041 ± 0.006	0.958	2.215 ± 0.006	0.574	2.599 ± 0.007	3.173 ± 0.010
587	1.127	2.007 ± 0.005	0.953	2.180 ± 0.005	0.571	2.563 ± 0.006	3.134 ± 0.009
723	1.118	1.965 ± 0.006	0.946	2.137 ± 0.006	0.567	2.516 ± 0.007	3.083 ± 0.010
874	1.108	1.919 ± 0.006	0.937	2.090 ± 0.006	0.561	2.466 ± 0.007	3.027 ± 0.010
				423 K			
sat.	1.276	2.533 ± 0.003	1.074	2.735 ± 0.003	0.642	3.167 ± 0.005	3.809 ± 0.007
48	1.262	2.508 ± 0.004	1.062	2.708 ± 0.004	0.635	3.135 ± 0.006	3.770 ± 0.008
121	1.254	2.461 ± 0.003	1.055	2.660 ± 0.004	0.630	3.085 ± 0.005	3.715 ± 0.007
196	1.247	2.415 ± 0.005	1.049	2.613 ± 0.005	0.627	3.035 ± 0.006	3.662 ± 0.008
277	1.238	2.371 ± 0.005	1.042	2.567 ± 0.006	0.622	2.987 ± 0.006	3.609 ± 0.007
363	1.233	2.325 ± 0.004	1.038	2.520 ± 0.005	0.620	2.938 ± 0.005	3.558 ± 0.007
448	1.227	2.283 ± 0.004	1.032	2.478 ± 0.005	0.616	2.894 ± 0.005	3.510 ± 0.008
539	1.218	2.247 ± 0.006	1.025	2.440 ± 0.006	0.612	2.853 ± 0.006	3.465 ± 0.008
636	1.211	2.211 ± 0.005	1.019	2.403 ± 0.006	0.608	2.814 ± 0.006	3.422 ± 0.009
773	1.199	2.165 ± 0.006	1.008	2.356 ± 0.006	0.602	2.762 ± 0.007	3.364 ± 0.009
920	1.187	2.119 ± 0.006	0.998	2.308 ± 0.007	0.595	2.710 ± 0.007	3.306 ± 0.010

Table 1 (continued)

p (bar)	$I = 1.0$ m		$I = 0.5$ m		$I = 0.1$ m		log K^0
	DHT	log Q	DHT	log Q	DHT	log Q	
			448 K				
sat.	1.394	2.788 ± 0.004	1.167	3.015 ± 0.004	0.694	3.488 ± 0.006	4.182 ± 0.007
52	1.361	2.766 ± 0.006	1.155	2.972 ± 0.005	0.686	3.441 ± 0.007	4.127 ± 0.009
133	1.347	2.704 ± 0.005	1.143	2.908 ± 0.006	0.679	3.372 ± 0.008	4.051 ± 0.009
213	1.337	2.644 ± 0.006	1.134	2.847 ± 0.005	0.674	3.307 ± 0.007	3.981 ± 0.008
309	1.325	2.580 ± 0.005	1.124	2.781 ± 0.006	0.668	3.237 ± 0.008	3.905 ± 0.010
393	1.316	2.530 ± 0.006	1.116	2.730 ± 0.006	0.663	3.183 ± 0.008	3.846 ± 0.009
486	1.308	2.480 ± 0.005	1.109	2.679 ± 0.005	0.659	3.129 ± 0.007	3.788 ± 0.008
585	1.298	2.432 ± 0.006	1.100	2.630 ± 0.006	0.653	3.077 ± 0.008	3.730 ± 0.009
684	1.291	2.396 ± 0.006	1.095	2.592 ± 0.006	0.650	3.037 ± 0.009	3.687 ± 0.010
817	1.276	2.346 ± 0.006	1.083	2.539 ± 0.007	0.642	2.980 ± 0.010	3.622 ± 0.011
951	1.264	2.303 ± 0.007	1.071	2.496 ± 0.007	0.635	2.932 ± 0.010	3.567 ± 0.011
			473 K				
sat.	1.534	3.027 ± 0.004	1.279	3.282 ± 0.004	0.757	3.804 ± 0.006	4.561 ± 0.008
60	1.512	2.966 ± 0.006	1.260	3.218 ± 0.006	0.745	3.733 ± 0.007	4.478 ± 0.010
146	1.489	2.887 ± 0.006	1.241	3.135 ± 0.006	0.734	3.642 ± 0.008	4.376 ± 0.011
231	1.473	2.812 ± 0.005	1.227	3.059 ± 0.006	0.726	3.560 ± 0.007	4.286 ± 0.010
326	1.461	2.736 ± 0.006	1.217	2.980 ± 0.007	0.719	3.478 ± 0.008	4.197 ± 0.011
428	1.447	2.668 ± 0.005	1.205	2.910 ± 0.006	0.712	3.403 ± 0.007	4.115 ± 0.011
528	1.435	2.606 ± 0.006	1.195	2.846 ± 0.007	0.706	3.335 ± 0.008	4.041 ± 0.010
632	1.423	2.544 ± 0.005	1.185	2.782 ± 0.007	0.700	3.267 ± 0.008	3.967 ± 0.011
732	1.412	2.499 ± 0.006	1.176	2.735 ± 0.007	0.694	3.217 ± 0.009	3.911 ± 0.012
863	1.400	2.452 ± 0.007	1.164	2.688 ± 0.008	0.687	3.165 ± 0.009	3.852 ± 0.011
975	1.386	2.429 ± 0.007	1.153	2.662 ± 0.008	0.681	3.134 ± 0.009	3.815 ± 0.012

Table 2. The partial molal volume of reaction (4) at different I, p, and T.

P (bar)	323 K	348 K	373 K	398 K	423 K	448 K	473 K
			$(\Delta\bar{V}^0)_{I=0}$	(cm^3 mol^{-1})			
sat.	21.4 ± 0.6	25.3 ± 0.6	31.1 ± 0.7	39.8 ± 0.8	53.7 ± 1.0	73.9 ± 1.1	93.1 ± 1.1
100	20.7 ± 0.8	24.7 ± 0.9	30.7 ± 1.0	37.9 ± 1.0	52.9 ± 1.1	72.5 ± 1.3	91.5 ± 1.2
200	20.0 ± 1.0	23.9 ± 1.0	30.3 ± 1.0	35.8 ± 1.1	51.7 ± 1.2	69.0 ± 1.4	89.6 ± 1.4
300	18.9 ± 1.0	22.9 ± 1.0	29.9 ± 1.1	33.6 ± 1.0	49.2 ± 1.3	62.7 ± 1.5	84.5 ± 1.4
400	17.7 ± 1.1	22.0 ± 1.1	27.6 ± 1.1	31.8 ± 1.1	46.5 ± 1.3	55.5 ± 1.4	74.8 ± 1.5
500	16.5 ± 1.1	21.1 ± 1.1	25.9 ± 1.0	30.7 ± 1.0	40.0 ± 1.4	47.5 ± 1.6	63.8 ± 1.4
600	15.7 ± 1.6	20.3 ± 1.1	24.1 ± 1.1	29.4 ± 1.2	34.7 ± 1.3	40.9 ± 1.6	55.8 ± 1.6
700			22.0 ± 1.7	28.5 ± 1.4	32.5 ± 1.4	37.5 ± 1.7	46.8 ± 1.7
800				24.8 ± 1.7	30.6 ± 1.7	34.2 ± 1.7	39.0 ± 1.7
900						27.3 ± 2.2	33.5 ± 2.1
			$(\Delta\bar{V})_{I=1.0\,m}$	(cm^3 mol^{-1})			
sat.	18.8 ± 0.6	22.2 ± 0.6	26.8 ± 0.7	35.8 ± 0.7	47.7 ± 1.0	63.6 ± 1.1	82.6 ± 1.1
100	17.5 ± 1.0	21.8 ± 1.0	26.4 ± 1.0	34.8 ± 1.1	46.7 ± 1.0	62.3 ± 1.2	81.8 ± 1.3
200	17.0 ± 1.2	20.4 ± 1.0	25.9 ± 1.1	33.5 ± 1.0	45.6 ± 1.3	59.5 ± 1.3	81.0 ± 1.4
300	16.6 ± 1.1	19.3 ± 1.1	25.7 ± 1.1	31.8 ± 1.1	41.4 ± 1.2	53.5 ± 1.4	68.1 ± 1.5
400	16.1 ± 1.3	18.7 ± 1.1	24.6 ± 1.0	30.2 ± 1.1	38.7 ± 1.4	44.3 ± 1.4	58.0 ± 1.4
500	15.6 ± 1.3	18.3 ± 1.0	23.4 ± 1.1	27.6 ± 1.0	35.2 ± 1.3	39.4 ± 1.5	51.4 ± 1.5
600	14.9 ± 1.6	17.8 ± 1.1	21.8 ± 1.1	25.7 ± 1.1	32.4 ± 1.3	38.0 ± 1.6	47.5 ± 1.6
700		15.5 ± 2.0	19.7 ± 1.7	24.2 ± 1.3	27.8 ± 1.4	35.9 ± 1.5	41.3 ± 1.6
800				21.1 ± 1.8	24.4 ± 1.7	28.7 ± 1.7	29.6 ± 1.8
900						21.5 ± 2.3	20.0 ± 2.2

Table 3. The values of a and b and the region of their validity.

T (K)	p (bar)	a_1 (J mol^{-1} K^{-1})	b_1 (J mol^{-1} K^{-2})	a_2 (J mol^{-1} K^{-1})	b_2 (J mol^{-1} K^{-2})
323–473	100	−138.0	−0.240	−110.0	−0.080
323–473	200	−136.5	−0.225	−107.0	−0.070
323–473	300	−136.0	−0.185	−106.1	−0.055
323–473	400	−132.8	−0.180	−105.1	−0.045
323–473	500	−132.1	−0.165	−103.0	−0.040
323–473	600	−131.5	−0.150	−101.0	−0.040
348–473	700	−136.5	−0.150	−101.5	−0.039
373–473	800	−142.0	−0.150	−102.0	−0.038
423–473	900	−155.0	−0.160	−103.0	−0.030

Table 4. The partial molal entropy of reaction (4) at different I, p, and T.

p (bar)	323 K	348 K	373 K	398 K	423 K	448 K	473 K
			$(\Delta\bar{S}^0)_{I=0}$ (J mol^{-1} K^{-1})				
100	138.0 ± 1.7	150.0 ± 1.3	162.0 ± 1.0	174.0 ± 1.1	186.0 ± 1.1	198.0 ± 1.1	210.0 ± 2.0
200	136.5 ± 1.8	147.7 ± 1.4	159.0 ± 1.1	170.2 ± 1.2	181.5 ± 1.2	192.7 ± 1.0	204.0 ± 1.9
300	136.0 ± 1.8	145.2 ± 1.3	154.5 ± 1.2	163.7 ± 1.0	173.0 ± 1.1	182.2 ± 1.0	191.5 ± 2.0
400	132.8 ± 1.9	141.8 ± 1.4	150.8 ± 1.0	159.8 ± 1.1	168.8 ± 1.1	177.8 ± 1.1	186.8 ± 2.0
500	132.1 ± 1.8	140.3 ± 1.4	148.6 ± 1.2	156.8 ± 1.2	165.1 ± 1.2	173.3 ± 1.2	181.6 ± 1.8
600	131.0 ± 1.9	138.5 ± 1.3	146.0 ± 1.1	153.5 ± 1.2	161.0 ± 1.2	168.5 ± 1.3	176.0 ± 1.9
700		136.5 ± 1.7	144.0 ± 1.4	151.5 ± 1.3	159.0 ± 1.3	166.5 ± 1.3	176.0 ± 1.8
800			142.0 ± 1.7	149.5 ± 1.4	157.0 ± 1.4	164.5 ± 1.4	172.0 ± 1.9
900					155.0 ± 1.8	163.0 ± 1.5	171.0 ± 2.0
			$(\Delta\bar{S})_{I=1.0\,m}$ (J mol^{-1} K^{-1})				
100	110.0 ± 1.8	114.0 ± 1.2	118.0 ± 0.8	122.0 ± 0.7	126.0 ± 0.8	130.0 ± 0.7	134.0 ± 1.7
200	107.0 ± 1.7	110.5 ± 1.1	114.0 ± 1.0	117.5 ± 0.9	121.0 ± 0.9	124.5 ± 0.9	128.0 ± 1.6
300	106.1 ± 1.7	108.8 ± 1.0	111.6 ± 1.1	114.3 ± 1.0	117.1 ± 1.1	119.8 ± 1.0	122.6 ± 1.7
400	105.1 ± 1.8	107.3 ± 1.2	109.7 ± 1.2	111.9 ± 1.0	114.1 ± 1.1	116.3 ± 1.2	118.6 ± 1.6
500	103.0 ± 1.8	105.0 ± 1.1	107.0 ± 1.2	109.0 ± 1.1	111.0 ± 1.0	113.0 ± 1.1	115.0 ± 1.7
600	101.0 ± 1.7	103.0 ± 1.2	105.0 ± 1.1	107.0 ± 1.2	109.0 ± 1.1	111.0 ± 1.2	113.0 ± 1.7
700		101.5 ± 1.8	103.5 ± 1.2	105.5 ± 1.2	107.5 ± 1.1	109.5 ± 1.2	111.5 ± 1.6
800			101.0 ± 1.8	103.9 ± 1.3	105.8 ± 1.2	107.7 ± 1.3	109.6 ± 1.7
900					103.0 ± 1.9	104.5 ± 1.3	106.0 ± 1.9

temperatures as functions of $P/(1+bp)$. Figure 2 shows that straight lines are obtained for $T \leq 373$ K. At higher temperatures the linear part of the curves decreases with increasing T. However $\Delta\bar{V}^0$ and $(\Delta\bar{V})_{1.0\,m}$ at saturation pressure were calculated from the slopes of the linear parts of the plots and are given in Table 2.

Figure 3 shows $\Delta\bar{G}^0$ and $\Delta\bar{G}_{1.0\,m}$ as functions of temperature at different constant pressures. The isobaric temperature dependence of $\Delta\bar{G}^0$ and $\Delta\bar{G}_{1.0\,m}$ can be described to a good approximation by the empirical equations

$$\Delta\bar{G}^{0T} = \Delta\bar{G}^{0T_r} + a_1(T - T_r) + b_1(T - T_r)^2, \quad (14)$$

$$\Delta\bar{G}^{T}_{1.0\,m} = \Delta\bar{G}^{T_r}_{1.0\,m} + a_2(T - T_r) + b_2(T - T_r), \quad (15)$$

where T_r denotes a reference temperature. The coefficients a_1, a_2, b_1 and b_2 are determined graphically. Their values, as well as the temperature region in which they are valid are shown in Table 3. $\Delta\bar{S}^0$ and $(\Delta\bar{S})_{1.0\,m}$ of reaction (4) were obtained from the differentiation of (14) and (15) with respect to the temperature at constant pressure,

$$\Delta\bar{S}^0 = -(\partial\Delta\bar{G}^0/\partial T)_p = -[a_1 + 2b_1(T - T_r)], \quad (16)$$

$$\Delta\bar{S}_{1.0\,m} = -(\partial\Delta\bar{G}_{1.0\,m}/\partial T)_p = -[a_2 + 2b_2(T - T_r)], \quad (17)$$

as well as from the slopes of the curves in Figure 3. Their averaged values are shown in Table 4.

$\Delta\bar{H}$ is then calculated due to the fundamental equations (18)

$$\Delta\bar{H}^0 = \Delta\bar{G}^0 + T\,\Delta\bar{S}^0 = \Delta\bar{G}^0 - T[a_1 + 2b_1(T - T_r)],$$

$$\Delta\bar{H}_{1.0\,m} = \Delta\bar{G}_{1.0\,m} + T\,\Delta\bar{S}_{1.0\,m} = \Delta\bar{G}_{1.0\,m} - T[a_2 + 2b_2(T - T_r)] \quad (19)$$

and are given in Table 5.

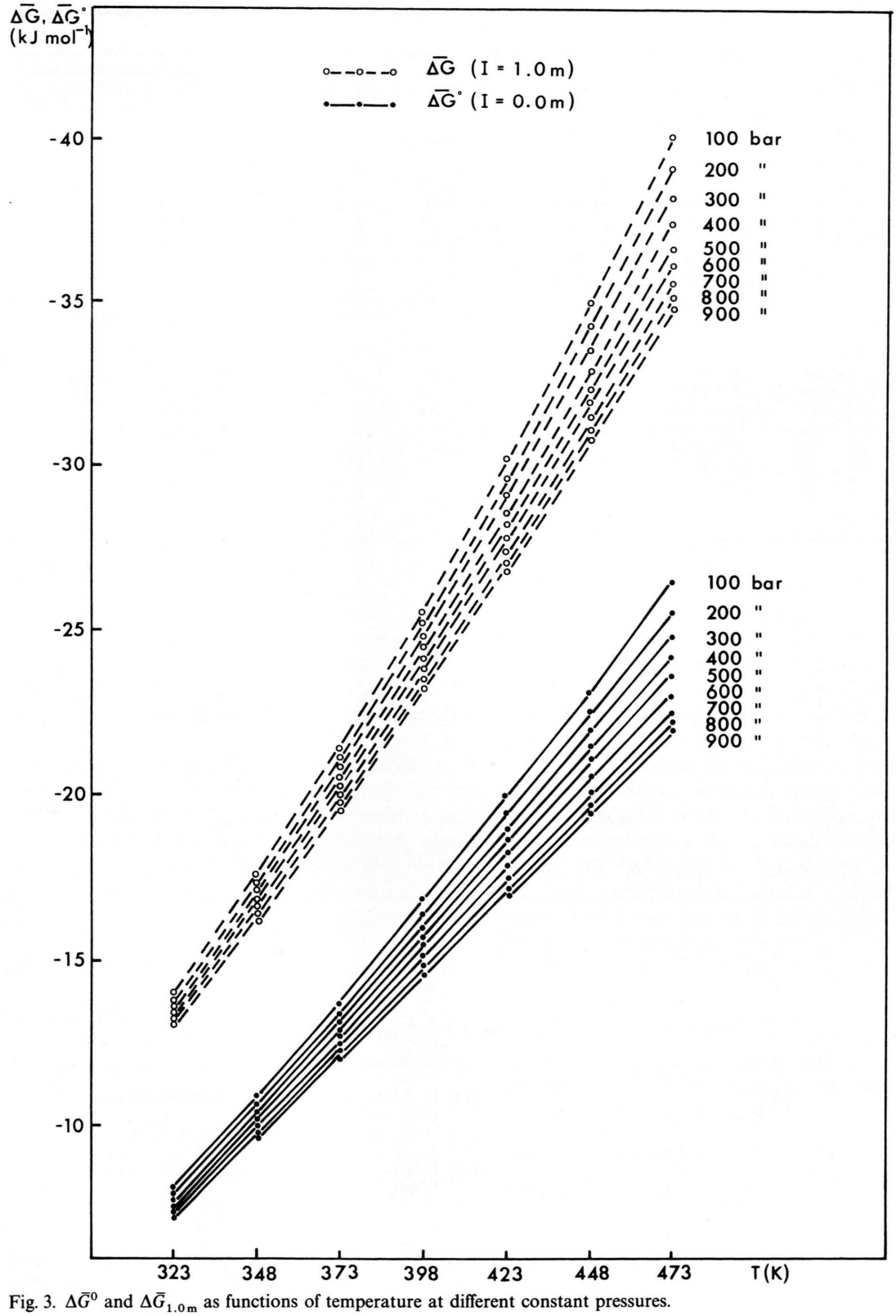

Fig. 3. $\Delta\bar{G}^0$ and $\Delta\bar{G}_{1.0\,m}$ as functions of temperature at different constant pressures.

Table 5. The partial molar enthalpy of reaction (4) at different I, p, and T.

p (bar)	323 K	348 K	373 K	398 K	423 K	448 K	473 K
			$(\Delta\bar{H}^0)_{I=0}$ (kJ mol^{-1})				
100	30.6 ± 0.6	34.6 ± 0.5	39.0 ± 0.4	43.6 ± 0.5	48.4 ± 0.5	53.7 ± 0.6	59.2 ± 1.0
200	30.3 ± 0.6	34.0 ± 0.5	38.2 ± 0.5	42.5 ± 0.5	47.1 ± 0.6	52.1 ± 0.5	57.3 ± 1.0
300	30.3 ± 0.6	33.4 ± 0.5	36.8 ± 0.5	40.3 ± 0.5	44.1 ± 0.5	48.1 ± 0.5	52.4 ± 1.0
400	29.5 ± 0.7	32.5 ± 0.6	35.7 ± 0.4	39.1 ± 0.5	42.7 ± 0.5	46.8 ± 0.6	50.9 ± 1.0
500	29.4 ± 0.7	32.2 ± 0.5	35.2 ± 0.5	38.3 ± 0.6	41.6 ± 0.6	45.3 ± 0.6	49.2 ± 0.9
600	29.3 ± 0.7	31.8 ± 0.5	34.5 ± 0.5	37.2 ± 0.5	40.3 ± 0.6	43.6 ± 0.7	47.1 ± 1.0
700		31.2 ± 0.7	34.0 ± 0.6	36.7 ± 0.6	39.8 ± 0.6	43.1 ± 0.7	46.7 ± 1.0
800			33.4 ± 0.7	36.3 ± 0.6	39.3 ± 0.7	42.6 ± 0.7	46.2 ± 1.0
900					38.7 ± 0.8	42.2 ± 0.8	46.1 ± 1.1
			$(\Delta\bar{H})_{I=1.0\,m}$ (kJ mol^{-1})				
100	27.4 ± 0.6	28.7 ± 0.5	30.3 ± 0.3	31.6 ± 0.3	33.3 ± 0.3	34.9 ± 0.3	36.8 ± 0.9
200	26.6 ± 0.6	27.7 ± 0.4	29.1 ± 0.4	30.4 ± 0.4	31.7 ± 0.4	33.1 ± 0.5	35.0 ± 0.8
300	26.5 ± 0.6	27.4 ± 0.4	28.5 ± 0.4	29.4 ± 0.4	30.5 ± 0.5	31.6 ± 0.5	33.2 ± 0.9
400	26.4 ± 0.6	27.0 ± 0.4	28.0 ± 0.5	28.8 ± 0.4	29.6 ± 0.5	30.6 ± 0.6	31.9 ± 0.8
500	25.8 ± 0.6	26.4 ± 0.4	27.2 ± 0.5	27.9 ± 0.5	28.7 ± 0.5	29.5 ± 0.5	30.8 ± 0.9
600	25.4 ± 0.6	25.9 ± 0.5	26.7 ± 0.5	27.4 ± 0.5	28.2 ± 0.5	29.0 ± 0.6	30.5 ± 0.8
700		25.6 ± 0.7	26.4 ± 0.5	27.0 ± 0.5	27.8 ± 0.5	28.7 ± 0.6	30.1 ± 0.8
800			26.0 ± 0.7	26.6 ± 0.6	27.4 ± 0.6	28.2 ± 0.6	29.6 ± 0.9
900					26.4 ± 0.8	27.0 ± 0.6	28.1 ± 1.0

The formation constants of reaction (4) increase with increasing temperature, but decreases with increasing pressure. This behaviour is understandable if an electrostatic model for the formation of HSO_4^- is considered, due to the decrease of the dielectric constant of water with increasing T and its (moderate) increase with increasing p. However, the volume reduction of the system accompanying the pressure increase is distinctly obtained due to a higher degree of electrostriction which takes place when more charged species are produced by dissociation. The partial molal volume of reaction (4) consequently decreases with increasing pressure, but increases with the temperature. ($\Delta\bar{V}^0$) values at given pressure and temperature are, therefore, higher than those in presence of interionic interaction. An extrapolation of $\Delta\bar{V}^0$ values at saturation pressures ($T \leq 373$ K) down to that at 298 K yields about 19 cm^3 mol^{-1}, which is in good agreement with the value obtained by Rohwer et al. [16] (20 ± 1 cm^3 mol^{-1}).

The extrapolation of $\Delta\bar{S}^0$ and $\Delta\bar{S}$ as well as $\Delta\bar{H}^0$ and $\Delta\bar{H}$ values to saturation pressure at the different temperatures yields a very good agreement with the values obtained in [9]. The observed decrease of the entropy with increasing pressure is again due to the increasing order in the system because of the higher electrostriction.

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