

Zu den pseudobinären Zustandssystemen Bi_2Ch_3 - BiX_3 und den ternären Phasen auf diesen Schnitten ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), I: Bismutsulfidhalogenide

The Pseudobinary Systems Bi_2Ch_3 - BiX_3 and the Ternary Phases on their Boundary Lines
($\text{Ch} = \text{S}, \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), I: Bismuth Sulfide Halides

Heinrich Oppermann^a und Uwe Petasch^b

^a Institut für Anorganische Chemie der Technischen Universität Dresden,
Mommsenstr. 13, D-01069 Dresden

^b Fraunhofer-IKTS, D-01277 Dresden

Sonderdruckanforderungen an Prof. Dr. Dr. h. c. H. Oppermann. E-mail:
ilona.salzmann@chemie.tu-dresden.de

Z. Naturforsch. **58b**, 725 – 740 (2003); eingegangen am 31. März 2003

The phase diagrams of the systems Bi_2S_3 - BiX_3 were constructed from results of DTA and total pressure measurements and x-ray analysis. The phases: BiSCl , $\text{Bi}_4\text{S}_5\text{Cl}_2$ and $\text{Bi}_{19}\text{S}_{27}\text{Cl}_3$ for $\text{X} = \text{Cl}$; BiSBr and $\text{Bi}_{19}\text{S}_{27}\text{Br}_3$ for $\text{X} = \text{Br}$; BiSI and $\text{Bi}_{19}\text{S}_{27}\text{I}_3$ for $\text{X} = \text{I}$ exist on the boundary lines. The enthalpies of formation and standard entropies of the phases follow from the coexistence decomposition pressure functions. The data are:

$\Delta H^\circ_B(\text{BiSCl}_{f,298})$	=	$-49,6 \pm 1,6$ kcal/mol	$S^\circ(\text{BiSCl}_{f,298})$	=	$30,3 \pm 2,5$ cal/K·mol
$\Delta H^\circ_B(\text{Bi}_4\text{S}_5\text{Cl}_{2,f,298})$	=	$-144,4 \pm 3$ kcal/mol	$S^\circ(\text{Bi}_4\text{S}_5\text{Cl}_{2,f,298})$	=	$114,0 \pm 4,6$ cal/K·mol
$\Delta H^\circ_B(\text{Bi}_{19}\text{S}_{27}\text{Cl}_{3,f,298})$	=	-520 ± 10 kcal/mol	$S^\circ(\text{Bi}_{19}\text{S}_{27}\text{Cl}_{3,f,298})$	=	490 ± 10 cal/K·mol
$\Delta H^\circ_B(\text{BiSBr}_{f,298})$	=	$-40,2 \pm 1,4$ kcal/mol	$S^\circ(\text{BiSBr}_{f,298})$	=	$32,0 \pm 3$ cal/K·mol
$\Delta H^\circ_B(\text{Bi}_{19}\text{S}_{27}\text{Br}_{3,f,298})$	=	$-493,6 \pm 6,7$ kcal/mol	$S^\circ(\text{Bi}_{19}\text{S}_{27}\text{Br}_{3,f,298})$	=	$499,8 \pm 17$ cal/K·mol
$\Delta H^\circ_B(\text{BiSI}_{f,298})$	=	$-27,8 \pm 1,4$ kcal/mol	$S^\circ(\text{BiSI}_{f,298})$	=	$36,1 \pm 2,5$ cal/K·mol
$\Delta H^\circ_B(\text{Bi}_{19}\text{S}_{27}\text{I}_{3,f,298})$	=	$-464,4 \pm 15$ kcal/mol	$S^\circ(\text{Bi}_{19}\text{S}_{27}\text{I}_{3,f,298})$	=	$502,7 \pm 15$ cal/K·mol

Key words: Bismuth Sulfide Halides, Phase Diagrams, Barograms, Total Pressure Measurements, Thermodynamic Data