

Table S1 Compilation of the thermodynamic data used in the model calculations.

	$\Delta_f H^0_{298}/$ $\text{kJ}\cdot\text{mol}^{-1}$	$S^0_{298}/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C^0_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = a + b\cdot 10^{-3}\cdot T + c\cdot 10^6\cdot T^{-2} + d\cdot 10^{-6}\cdot T^2$				reference
			a	b	c	d	
B(s)	0	5.8	18.87	8.17	-0.93	-1.36	[1]
B(g)	560.0	153.4	28.8	-	-	-	[1]
B ₂ (g)	829.7	202.0	31.6	-	-	-	[1]
BBr(g)	234.0	225.0	36.21	1.15	-0.34	-	[1]
BBr ₃ (g)	-204.2	324.3	80.38	1.44	-1.19	-	[1]
Br(g)	111.9	175.0	19.87	1.49	0.04	-	[1]
Br ₂ (g)	32.2	249.4	37.03	0.88	-0.11	-	[1]
Co(s)	0	30.1	19.13	20.47	-4.68	-	[1]
CoBr ₂ (g)	0.3	321.1	67.57	0	-0.39	-	$\Delta_f H^0$ calculated on basis of [2], S^0 and C^0_p from NiBr ₂ (g) [1]
Co ₂ B(s)	-125.5	59.8	60	-	-	-	[1]
CoB(s)	-94.1	30.5	34.6	-	-	-	[1]

Calculation of $\Delta_f H^0_{298}(\text{CoBr}_2(\text{g}))$:



$$\Delta_{\text{subl}} H^0_{298} = \Delta_f H^0_{298}(\text{CoBr}_2(\text{g})) - \Delta_f H^0_{298}(\text{CoBr}_2(\text{s}))$$

$$\Delta_f H^0_{298}(\text{CoBr}_2(\text{s})) = -215.7 \text{ kJ}\cdot\text{mol}^{-1} [1]$$

$$\Delta_f H^0_{298}(\text{CoBr}_2(\text{g})) = 216 \text{ kJ}\cdot\text{mol}^{-1} + (-215.7 \text{ kJ}\cdot\text{mol}^{-1}) = 0.3 \text{ kJ}\cdot\text{mol}^{-1}$$

[1] M. Binnewies, E. Milke, *Thermochemical Data of Elements and Compounds*, Wiley, VCH, Weinheim, 2nd Ed. 2002.

[2] G. Bardi, B. Brunetti, E. Ciccariello, V. Piacente, *J. Alloy. Compd.*, 1997, **247**, 202.