

## Revised Thermodynamic Description for the Co-Mo System

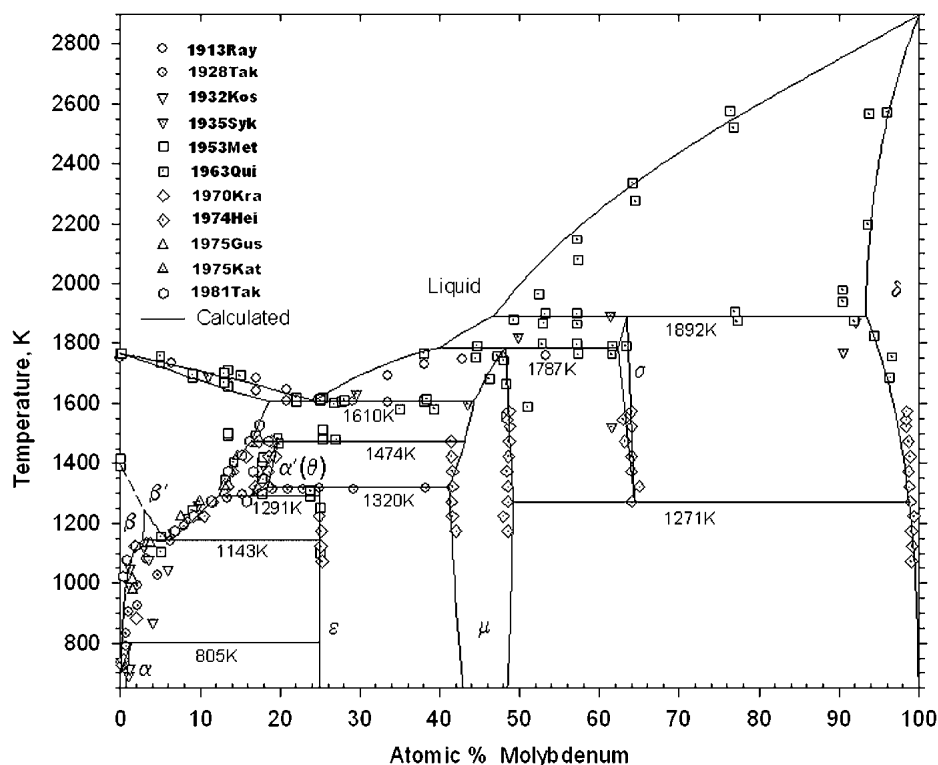
The previously assessed Co-Mo system [1999Dav] has been partially revised: thermodynamic descriptions for the liquid,  $\mu$ ,  $\sigma$ , and bcc phases were amended in the attempt to eliminate some unrealistic phase diagram features, such as an inverse liquid miscibility gap and an extended metastable homogeneity range for the  $\sigma$ -phase.

The previous thermodynamic assessment of the Co-Mo system by the present authors adequately reproduces the evaluated phase diagram and thermochemical data for all the phases [1999Dav]. However, the original description resulted in the formation of an implausible inverse miscibility gap in the liquid at high temperatures [2001Che]. The presence of an inverted miscibility gap was not noticed during the assess-

ment since the minimum miscibility temperature of 3022 K was above the melting points of all the solid phases in the system and thus did not appear on the diagram calculated in the 300-3000 K temperature range. Although posing no problem for the Co-Mo binary description, the liquid immiscibility could potentially manifest itself in the higher-order systems with high-melting components. In addition to that, thorough examination of various metastable equilibria revealed that in the absence of  $\mu$  and  $\varepsilon$  intermetallics, the  $\sigma$  phase homogeneity range extended unrealistically far into the Co-rich corner of the phase diagram. Also, the ordering on the sublattices in the  $\mu$ -phase models appeared to have questionable temperature behavior (the degree of ordering was slightly increasing with temperature).

This prompted the authors to amend the description of the aforementioned phases as summarized in Table 1. Recalculated thermochemical quantities of the intermetallic compounds are presented in Table 2. Note that Tables 1 and 2, including labeling of all the phases, model parameters, equations, and references, correspond to Tables 4 and 5 in [1999Dav], respectively. The phase diagram calculated using the modified descriptions is given in Fig. 1 with symbols, legends, and references corresponding to those from Fig. 1 in [1999Dav].

The phase diagram appears essentially unchanged, with the invariant temperatures deviating from the previous assessment by a maximum of four degrees for the liquid +  $\sigma \leftrightarrow \mu$  peritectic, which is still well within experimental uncertainty. At the same



**Fig. 1** Experimental and calculated phase diagram for the Co-Mo system:  $\alpha$ , ferro-cph (Co);  $\alpha'(\theta)$ , para-cph (Co);  $\beta$ , ferro-fcc (Co);  $\beta'$ , para-fcc (Co);  $\delta$ , bcc (Mo);  $\varepsilon$ ,  $\mu$ , and  $\sigma$ , intermetallic compounds; Model II ( $\sigma$  phase) and Model V ( $\mu$  phase) are used for calculations; symbols and legends are from [1999Dav].

**Table 1 Model Parameters for the Co-Mo System (Re-optimized Parameters Are Given in Bold)**

Phase	Model (Eq. No.) (a)	Parameter	$a_i$	$b_i$	$c_i$
Liquid	Redlich-Kister (Eq 5)	${}^0L_{\text{Co,Mo}}$	<b>-68 756.05</b>	<b>31.80</b>	<b>0.2</b>
		${}^1L_{\text{Co,Mo}}$	<b>2 184.77</b>	<b>1.50</b>	
cph $\alpha$	Redlich-Kister (Eq 5, 11, 12)	${}^0L_{\text{Co,Mo}}$	-29 315.7	23.755	
		${}^1L_{\text{Co,Mo}}$	-27 975.9	-1.936	
		${}^2L_{\text{Co,Mo}}$	24 698.3	0.000	
		${}^0T_{\text{Co}}, {}^0\beta_{\text{Co}}$	1 396	1.350	
		${}^0T_{\text{Co,Mo}}, {}^0\beta_{\text{Co,Mo}}$	-1 000	0.000	
fcc $\beta$	Redlich-Kister (Eq 5, 11, 12)	${}^0L_{\text{Co,Mo}}$	-29 557.1	10.953	
		${}^1L_{\text{Co,Mo}}$	-1 382.2	15.371	
		${}^2L_{\text{Co,Mo}}$	-18 135.4	0.000	
		${}^0T_{\text{Co}}, {}^0\beta_{\text{Co}}$	1 396	1.350	
		${}^0T_{\text{Co,Mo}}, {}^0\beta_{\text{Co,Mo}}$	-3 700	-3.578	
bcc $\delta$	Redlich-Kister (Eq 5, 11, 12)	${}^0L_{\text{Co,Mo}}$	<b>5 000</b>	7.597	
		${}^1L_{\text{Co,Mo}}$	<b>-19 208.67</b>	0.000	
		${}^0T_{\text{Co}}, {}^0\beta_{\text{Co}}$	1 450	1.350	
		${}^0T_{\text{Co,Mo}}, {}^0\beta_{\text{Co,Mo}}$	-3 700	-3.445	
		$\Delta^f G$	-47 009.6	20.816	
$\varepsilon$	line compound (Eq 13)	$\Delta^f G$	-47 009.6	20.816	
$\sigma$	$(\text{Co})_8(\text{Mo})_4(\text{Co,Mo})_{18}$ (Model I, Eq 14)	$\Delta^f G_{\text{Co:Mo:Co}}$	<b>-130 932.67</b>	<b>240.554</b>	
		$\Delta^f G_{\text{Co:Mo:Mo}}$	<b>-87 868.24</b>	<b>14.662</b>	
		${}^0L_{\text{Co:Mo:Co,Mo}}$	<b>-157 492.37</b>	<b>0</b>	
$\sigma$	$(\text{Co})_{10}(\text{Mo})_4(\text{Co,Mo})_{16}$ (Model II, Eq 14)	$\Delta^f G_{\text{Co:Mo:Co}}$	<b>-287 355.10</b>	<b>295.453</b>	
		$\Delta^f G_{\text{Co:Mo:Mo}}$	<b>-114 357.37</b>	<b>-2.477</b>	
		${}^0L_{\text{Co:Mo:Co,Mo}}$	<b>134 706.57</b>	<b>0</b>	
$\mu$	$(\text{Co,Mo})_7(\text{Co,Mo})_6$ (Model III, Eq 14)	$\Delta^f G_{\text{Co:Mo}}$	-105 406.7	19.784	
		$\Delta^f G_{\text{Co:Co}}$	65 000.0	0.000	
		$\Delta^f G_{\text{Mo:Mo}}$	65 000.0	0.000	
		$\Delta^f G_{\text{Mo:Co}}$	235 406.7	-19.784	
		${}^0L_{\text{Co,Mo:Mo}}$	<b>-56 408.1</b>	<b>159.000</b>	
		${}^0L_{\text{Co,Mo:Co}}$	<b>-56 408.1</b>	<b>159.000</b>	
		${}^0L_{\text{Co:Co,Mo}}$	<b>-286 332.5</b>	<b>259.000</b>	
		${}^0L_{\text{Mo:Co,Mo}}$	<b>-286 332.5</b>	<b>259.000</b>	
		$\Delta^f G_{\text{Co:Mo:Mo}}$	-105 406.7	19.784	
		$\Delta^f G_{\text{Co:Mo:Co}}$	-64 478.6	49.936	
$\mu$	$(\text{Co,Mo})_7(\text{Mo})_2(\text{Co,Mo})_4$ (Model IV, Eq 14)	$\Delta^f G_{\text{Mo:Mo:Mo}}$	65 000.0	0.000	
		$\Delta^f G_{\text{Mo:Mo:Co}}$	105 928.1	30.152	
		${}^0L_{\text{Co,Mo:Mo:Mo}}$	<b>-59 132.6</b>	<b>161.000</b>	
		${}^0L_{\text{Co,Mo:Mo:Co}}$	<b>-59 132.6</b>	<b>161.000</b>	
		${}^0L_{\text{Co:Mo:Co,Mo}}$	<b>-117 092.4</b>	<b>115.000</b>	
		${}^0L_{\text{Mo:Mo:Co,Mo}}$	<b>-117 092.4</b>	<b>115.000</b>	
		$\Delta^f G_{\text{Co:Co:Mo:Mo}}$	-105 406.7	19.784	
		$\Delta^f G_{\text{Co:Co:Mo:Co}}$	-130 245.8	57.602	
		$\Delta^f G_{\text{Co:Mo:Mo:Mo}}$	-87 000.0	15.000	
		$\Delta^f G_{\text{Co:Mo:Mo:Co}}$	-111 839.1	52.818	
$\mu$	$(\text{Co})_6(\text{Co,Mo})_1(\text{Mo})_4(\text{CoMo})_2$ (Model V, Eq 14)	${}^0L_{\text{Co:Co,Mo:Mo:Co}}$	<b>-4 263.0</b>	<b>10.000</b>	
		${}^0L_{\text{Co:Co,Mo:Mo:Mo}}$	<b>-4 263.0</b>	<b>10.000</b>	
		${}^0L_{\text{Co:Co:Mo:Co,Mo}}$	<b>-8 141.0</b>	<b>20.000</b>	
		${}^0L_{\text{Co:Mo:Mo:Co,Mo}}$	<b>-8 141.0</b>	<b>20.000</b>	
		$\Delta^f G_{\text{Co:Co:Mo:Mo}}$	-105 406.7	19.784	
		$\Delta^f G_{\text{Co:Co:Mo:Co}}$	-130 245.8	57.602	
		$\Delta^f G_{\text{Co:Mo:Mo:Mo}}$	-87 000.0	15.000	

(a) Models and equations are from [1999Dav]; the  $a_i$  and  $b_i$  coefficients for the  $G$  and  $L$  parameters are in J/mol and J/mol K, respectively;  $T_c$  in K, and  $\beta$  in Bohr magnetons.

time, the descriptions for the liquid,  $\sigma$ , and  $\mu$  models were improved. Even though it was not possible to eliminate the appearance of the inverse liquid miscibility gap at high

temperatures, its critical temperature was “pushed up” to 3965 K compared with 3022 K in [1999Dav]. The calculated metastable phase boundaries of the  $\sigma$  phase for the  $\sigma + \beta/\beta'$  and

$\sigma + \alpha/\alpha'$  equilibria became more realistic for both models\* I and II and

\*The details of the models may be found in the original publication [1999Dav].

**Table 2** Calculated Thermodynamic Properties of the Intermetallic Compounds (Calculated Quantities That Differ From [1999Dav] Are Given in Bold)

Phase	$x$ , at.% Mo	$T_{\text{melt.}}$ , K	$\Delta_f H^{298}$ , J/mol at	$\Delta_f S^{298}$ , J/mol at K	$\Delta_f H^{298}$ [1980Bre] J/mol at	$\Delta_f S^{298}$ [1980Bre] J/mol at K
$\epsilon$	25	<b>1320(a)</b>	-5360	0.1	-5300 $\pm$ 1200	-1.3 $\pm$ 0.8
$\mu$	48	<b>1787</b>	<b>-3434</b>	<b>2.5</b>	-3800 $\pm$ 400	1.8 $\pm$ 0.8
$\sigma$	63	<b>1892</b>	<b>-711</b>	<b>2.1</b>	-1900 $\pm$ 2500	3.3 $\pm$ 1.2

(a) peritectoid decomposition

had a tendency to approach the “ideal” stoichiometric composition of 66.7 at.% Mo with decreasing temperature. Ordering on the sublattices in the  $\mu$  phase for all three models, III, IV and V, has a more realistic temperature trend as it slightly decreases with increasing temperature. It should be noted, however, that no experimental data for the site occupancies in the  $\mu$  phase exist in the literature to validate the temperature dependence of the ordering behavior produced by the present modeling.

In conclusion, the authors recommend replacing the Co-Mo description in [1999Dav] with the present one. The revised description should be used with caution for calculations at temperatures above approximately 3700 K, especially in multicomponent systems, to avoid appearance of an inverse liquid miscibility gap.

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