




Titel Ailments of PMATCHC with Respect to Temperature Extrapolations, and Suggested Cures

Autor Tres Thoenen

Abstract:

The present version of PMATCHC (as described in TM-44-01-07) makes implicit assumptions for the temperature dependence of equilibrium constants if not enough heat capacity data are available for a rigorous calculation.

This communication proposes a modified calculation scheme for a next incarnation of PMATCHC avoiding any implicit assumptions which may lead to erroneous values of heat capacities of formation from the elements.

Abt.	Empfänger / Empfängerinnen	Expl.	Abt.	Empfänger / Empfängerinnen	Expl.		Expl.							
01	M. Jermann	1	Nagra	B. Schwyn P. Wersin P. Zuidema Bibliothek	1	Bibliothek	3							
40	W. Kröger	1			1	Reserve	5							
44	U. Berner	1			1	Total	23							
	E. Curti	1	New Bern	F. J. Pearson	1	Seiten	13							
	J. Hadermann	1				Beilagen	-							
	W. Hummel	1				Informationsliste								
	D. Kulik	1				D	1	2	3	4	5	8	9	A
	T. Thoenen	3				Visum Abt./Laborleitung:								

For the purposes of the Nagra/PSI Thermochemical Data Base update (Nagra/PSI TDB Version 01/01, HUMMEL et al. 2001) it was decided to concentrate on the evaluation of thermochemical data at 25°C. Therefore, no special efforts were made to gather data on the temperature dependence of equilibrium constants. This is reflected in the kind of data entered in PMATCHC, see Table 1. For the majority of secondary master species, aqueous product species, solids and gases (counting beans: 268 of a total 456, or 59%) only $\log K^\circ$ was entered and in an additional 101 cases only $\log K^\circ$ and either $\Delta_r H_m^\circ$ or $\Delta_r S_m^\circ$. Thus, for 369 of the 456 equilibria represented in the database (81%) there is no heat capacity information that would enable the rigorous extrapolation of equilibrium constants to temperatures higher than 25°C.

In the present version of PMATCHC (PEARSON et al. 2001) the following assumptions are made if not enough heat capacity data are entered to represent the temperature dependence of an equilibrium constant (compare with Table 2 in PEARSON et al. 2001):

1) **Calculation cases 10, 15, 16, 17, 21a, and 22a:**

If only $\log K^\circ$, $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ of an equilibrium are known but no heat capacity data are given, it is assumed that $\Delta_r C_{p,m}^\circ$ is zero and that it remains zero at any temperature (as a consequence $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ are also set to zero, see eq. 3.1 in the Appendix). This ultimately leads to the integrated van't Hoff equation (also called two-term approximation) for the temperature dependence of the equilibrium constant and only the coefficients A and C of the temperature-dependent $\log K$ expression, see eq. (3.2) in the Appendix, are non-zero.

If $\Delta_r C_{p,m}^\circ$, or $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$, see eq. (3.1a) in the Appendix, are known for all master species participating in the reaction, values for the corresponding entities of the product species (aqueous product species, solid or gas) can be calculated from $\Delta_r C_{p,m}^\circ = \Delta_r a = \Delta_r b = \Delta_r c = 0$.

Note that in this case, the values calculated for $\Delta_r C_{p,m}^\circ$, $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ depend on how the formation reaction is written (i.e. which master species are used)! However, $\Delta_r C_{p,m}^\circ$, $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ are properties of formation from the elements and **should be independent from how the formation reaction from master species is formulated. These values are therefore dubious and are only correct if it can be shown that $\Delta_r C_{p,m}^\circ$ of the formation reaction from the master species is actually zero or nearly so.**

2) **Calculation cases 9, 116d, 21b, and 22b:**

If only $\log K^\circ$, $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$, $\Delta_r S_m^\circ$, and $\Delta_r C_{p,m}^\circ$ of an equilibrium are known but no further heat capacity data are given, it is assumed that $\Delta_r C_{p,m}^\circ$ is constant with temperature (as a consequence, $\Delta_r a$ is set to $\Delta_r C_{p,m}^\circ$, and $\Delta_r b$ and $\Delta_r c$ are both set to zero). This leads to the three-term approximation of temperature dependence and only A, C, and D are non-zero.

If $\Delta_r C_{p,m}^\circ$, or $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ are known for all master species participating in the reaction, values for the corresponding entities of the product species can be calculated from $\Delta_r C_{p,m}^\circ = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$. These values of the product species are only correct if it can be shown that the three-term approximation gives a reasonable representation of the temperature dependence of the equilibrium constant.

3) **Calculation cases 14, 117d, and 17a:**

If only $\log K^\circ$, $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$, and $\Delta_r S_m^\circ$ of an equilibrium are known, as well as $\Delta_r C_{p,m}^\circ$ of the product species and $\Delta_r a$, $\Delta_r b$, $\Delta_r c$, and $\Delta_r C_{p,m}^\circ$ of all master species involved in the reaction, it is assumed that $\Delta_r C_{p,m}^\circ$ for the product species is constant with temperature. As a consequence, $\Delta_r a$ for the product species is set to $\Delta_r C_{p,m}^\circ$, and $\Delta_r b$ and $\Delta_r c$ are both set to zero. If $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ are known for all master species involved in the formation reaction of the product species, $\Delta_r a$, $\Delta_r b$, $\Delta_r c$, and $\Delta_r C_{p,m}^\circ$ can be calculated.

Note that these calculation cases were not used in the preparation of the Nagra/PSI TDB Version 01/01.

4) **Calculation cases 18, 19, and 20:**

If only $\log K^\circ$ and $\Delta_r G_m^\circ$ of an equilibrium are known, all other properties of reaction are left blank. All temperature coefficients of the heat capacity equations are left blank except A, which is set to $\log K^\circ$.

All aqueous species, solids and gases in the Nagra/PSI TDB Version 01/01 for which thermodynamic data were calculated according to the calculation cases discussed above (except cases 18, 19, and 20) are listed in Table 2.

In my opinion it is not desirable that the Nagra/PSI TDB contains a) data based on implicit assumptions or b) heat capacities of formation from the elements that depend on how the formation reaction from master species is formulated.

In order to avoid this, I propose a modified calculation scheme which is summarized in Table 3. The calculation cases discussed above are modified as follows:

1 mod.) **Calculation cases 10, 15, 16, 17, 21a, and 22a:**

$\Delta_r C_{p,m}^\circ$, $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ are left blank and consequently also $\Delta_r C_{p,m}^\circ$, $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ of the product species. As no temperature dependence of the equilibrium constant can be derived from these data, A, B, C, D, and E are also left blank.

2 mod.) **Calculation cases 9, 116d, 21b, and 22b:**

$\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ are left blank and consequently also $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ of the product species. As no temperature dependence of the equilibrium constant can be derived from these data, A, B, C, D, and E are also left blank.

3 mod.) **Calculation cases 14, 117d, and 17a:**

$\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ for the product species are left blank and therefore also $\Delta_r a$, $\Delta_r b$, $\Delta_r c$. As no temperature dependence of the equilibrium constant can be derived from the data, A, B, C, D, and E are also left blank.

4 mod.) **Calculation cases 18, 19, and 20:**

Only $\log K^\circ$ and $\Delta_r G_m^\circ$ of an equilibrium are known. From these data, no temperature dependence of the equilibrium constant can be derived. In order to be consistent with the modified calculation cases discussed in 1 mod.), 2 mod.), and 3 mod.), A should also be left blank (instead of being set to $\log K^\circ$).

Note, however, that the present version of PMATCHC is flexible enough to make explicit assumptions for the temperature dependence of equilibrium constants:

- The three-term approximation described in 2) can be made explicit by entering the known value of the heat capacity of reaction at 25°C not into $\Delta_r C_{p,m}^\circ$ (D25CPR) but into $\Delta_r a$ (DACPR). PMATCHC then sets $\Delta_r b = \Delta_r c = 0$ and thus $\Delta_r C_{p,m}^\circ = \Delta_r a$, and further calculations are made as described in 2). Thus, given the heat capacity of reaction at 25°C, one can enforce the three-term approximation by entering the corresponding value into DACPR (as, e.g., in calculation case 8) or avoid it by entering the value into D25CPR (as in the modified calculation case 9).
- The two-term approximation described in 1) can be made explicit by entering a value of 0 for $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$. As a consequence, $\Delta_r C_{p,m}^\circ = 0$ and further calculations are made as described in 1). Thus, given no heat capacity data, one can enforce the two-term approximation by entering a value of 0 for $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ (as, e.g., in calculation case 6) or avoid it by leaving $\Delta_r a$, $\Delta_r b$, $\Delta_r c$, and $\Delta_r C_{p,m}^\circ$ blank (as in the modified calculation case 10).

- If only $\log K^\circ$ or $\Delta_r G_m^\circ$ of an equilibrium is known, the one-term approximation can be made by entering a value of 0 for $\Delta_r S_m^\circ$, $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ (as, e.g., in calculation case 6). As a consequence, only C of the corresponding $\log K$ expression is non-zero. Note that the calculation cases 18, 19, and 20 (be they modified or not) do not correspond to the one-term approximation.

The proposed modified calculation scheme discussed above may appear too puristic for practical purposes. It does not allow the temperature extrapolation of equilibrium constants if there are no heat capacity data entered (either measured or explicitly based on the above mentioned assumptions) because in that case the coefficients A, B, C, D, and E of the temperature-dependent $\log K$ expression are left blank.

As a compromise between purism and practicability one may consider the calculation scheme proposed in Table 4. The calculations are made as in Table 3, thereby retaining the practice of not calculating heat capacities based on any implicit assumptions. However, if there are enough data available for the two-term or the three-term extrapolation, the corresponding coefficients of the temperature-dependent $\log K$ expression (A and C for the two-term and A, C, and D for the three-term extrapolation) are calculated. In order to signify that the calculation of these parameters is based on assumptions, the remaining coefficients are left blank.

ACKNOWLEDGMENTS

This note benefitted from many fruitful and (sometimes) heated discussions with F.J. PEARSON and D. KULIK. Many thanks to F.J. PEARSON for useful comments on an earlier version of the manuscript and to the suggestion of a compromise version of the calculation scheme. Thanks to W. HUMMEL for pointing out some overly extreme statements.

REFERENCES

- HUMMEL W., BERNER U., CURTI E., PEARSON F.J. & THOENEN T. (2001) Nagra/PSI Thermochemical Data Base 01/01. PSI Report and Nagra Technical Report, in peer-review.
- PEARSON F.J., THOENEN T., DMYTRIYEVA S., KULIK D.A. & HUMMEL W. (2001) PMATCHC: A Program to MANage ThermoCHEmical data, written in C++ (Version 1.1, 31-08-2001). Internal Report TM-44-01-07, Paul Scherrer Institut, Villigen, Switzerland.

Table 1: PMATCHC calculation cases (see PEARSON et al. 2001) used in preparation of the Nagra/PSI Thermochemical Data Base Version 01/01 (HUMMEL et al. 2001). The upper part of the table indicates the kind of data entered for each calculation case (E: entered; E*: two of three entered; E**: one of two entered). The lower part of the table indicates the numbers of species, gases and solids for which the respective calculation case was used.

		1	2	3	4	9	10	11	13	15	16	17	18	20	Total
A Coef. logK(T) expression	ALGK	E	E	E	E										
B Coef. logK(T) expression	BLGK	E	E												
C Coef. logK(T) expression	CLGK	E	E	E	E										
D Coef. logK(T) expression	DLGK	E	E	E											
E Coef. logK(T) expression	ELGK	E													
logK(25°C)	LGK25										E	E	E		
$\Delta_r G_m^0$	DGR					E*	E*								
$\Delta_r H_m^0$	DHR					E*	E*				E**				
$\Delta_r S_m^0$	DSR					E*	E*				E**				
$\Delta_f C_{p,m}^0$	D25CPR					E									
$\Delta_f a$: Maier-Kelley	DACPR														
$\Delta_f b$: Maier-Kelley	DBCPR														
$\Delta_f c$: Maier-Kelley	DCCPR														
$\Delta_f G_m^0$	GF							E*	E*	E*				E	
$\Delta_f H_m^0$	HF							E*	E*	E*		E**			
$\Delta_f S_m^0$	SF							E*	E*	E*		E**			
$\Delta_f C_{p,m}^0$	CP25F														
$\Delta_f a$: Maier-Kelley	CPAF							E	E						
$\Delta_f b$: Maier-Kelley	CPBF							E							
$\Delta_f c$: Maier-Kelley	CPCF							E							
Secondary Master Species		4				1		5		10	7	2	4		33
Product Species		8	1	1	1	3	2		1	5	81	6	212	2	323
Solids		14				1		2		11	12	1	52	1	94
Gases		5									1				6
Total		31	1	1	1	5	2	7	1	26	101	9	268	3	456

Table 2: List of aqueous species, solids and gases from the Nagra/PSI Thermochemical Data Base Version 01/01 (HUMMEL et al. 2001) which are affected by the shortcomings of the present version of PMATCHC. Species for which heat capacity data of formation from the elements are calculated (see text for a discussion) are set bold. The numbers refer to the calculation cases.

Secondary Master Species							
Al(OH)4-	9	Eu+2	15	Fe+3	16	U+4	17
		HS-	15	H2PO4-	16	UO2+	17
		Np+3	15	H3PO4	16		
		Np+4	15	NH3	16		
		NpO2+	15	PO4-3	16		
		Pu+3	15	SiO(OH)3-	16		
		Pu+4	15	SiO2(OH)2-2	16		
		PuO2+	15				
		S2O3-2	15				
		SO3-2	15				
Product Species							
Al(OH)2+	9	Fe(SO4)2-	16	NiSO4	16	SrSO4	16
Al(OH)3	9	Fe2(OH)2+4	16	Np(SO4)2	16	U(CO3)5-6	16
AlOH+2	9	Fe3(OH)4+5	16	NpF+3	16	U(SO4)2	16
		FeCl+2	16	NpO2(CO3)3-4	16	UC1+3	16
UF4	10	FeF+2	16	NpO2(CO3)3-5	16	UF+3	16
UOH+3	10	FeF2+	16	NpO2(SO4)2-2	16	UF2+2	16
		FeF3	16	NpO2SO4	16	UF3+	16
As(OH)4-	15	FeOH+	16	NpO2SO4-	16	UO2(CO3)2-2	16
AsO4-3	15	FeOH+2	16	NpSO4+2	16	UO2(CO3)3-4	16
H2AsO4-	15	FeSO4	16	Pu(SO4)2-	16	UO2(SO4)2-2	16
H3AsO4	15	FeSO4+	16	PuF+3	16	UO2C1+	16
HSO3-	15	H2S	16	PuF2+2	16	UO2C12	16
		H2SeO3	16	PuO2(CO3)2-2	16	UO2CO3	16
(UO2)3(CO3)6-6	16	HSeO3-	16	PuO2(CO3)3-4	16	UO2F+	16
AlF+2	16	KSO4-	16	PuO2(CO3)3-5	16	UO2F2	16
AlF2+	16	MgF+	16	PuO2(SO4)2-2	16	UO2F3-	16
AlF3	16	MgSO4	16	PuO2OH+	16	UO2F4-2	16
AlF4-	16	MnOH+	16	PuO2SO4	16	UO2SO4	16
AlF5-2	16	MnSO4	16	PuOH+3	16	USO4+2	16
AlF6-3	16	NaCO3-	16	PuSO4+	16		
CaF+	16	NaSO4-	16	RaCl+	16	Ni(OH)2	17
CaSO4	16	Ni2OH+3	16	RaCO3	16	Ni(OH)3-	17
Fe(OH)2+	16	Ni4(OH)4+4	16	RaOH+	16	ZrF+3	17
Fe(OH)3	16	NiOH+	16	RaSO4	16	ZrF2+2	17
Fe(OH)4-	16	NiP2O7-2	16	SeO4-2	16	ZrF3+	17
						ZrF4	17
Solids							
Gibbsite	9	Graphite	15	Brucite	16	Eu(OH)3(cr)	17
		Mo(cr)	15	Dolomite(dis)	16		
		Molybdite	15	Dolomite(ord)	16		
		Nb2O5(cr)	15	Hausmannite	16		
		NbO2(cr)	15	Kaolinite	16		
		Pd(cr)	15	NpO2OH(am,ag)	16		
		Quartz	15	NpO2OH(am,fr)	16		
		S(rhomb)	15	Portlandite	16		
		Se(cr)	15	Pyrolusite	16		
		Sn(cr)	15	RaCO3(cr)	16		
		Tugarinovite	15	RaSO4(cr)	16		
				SiO2(am)	16		
Gases							
H2S(g)	16						

Table 3: Summary of PMATCHC calculation cases. Suggested changes with respect to PEARSON et al. (2001) are shaded.

Property	PMATCHC Field Name	logK(T) Coefficients Entered				Properties of Reaction Entered				
		1	2	3	4	6	7	8	9	10
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	E	E	E	E	3.19	3.19	3.19	--	--
B Coef. logK(T) expression	BLGK	E	E	set to 0	set to 0	3.16	3.16	3.16 \Rightarrow 0	--	--
C Coef. logK(T) expression	CLGK	E	E	E	E	3.17	3.17	3.17	--	--
D Coef. logK(T) expression	DLGK	E	E	E	set to 0	3.15	3.15	3.15	--	--
E Coef. logK(T) expression	ELGK	E	set to 0	set to 0	set to 0	3.14	3.14 \Rightarrow 0	3.14 \Rightarrow 0	--	--
logK(25°C)	LGK25	3.2	3.2	3.2	3.2	3.2	3.2	3.2	2.1	2.1
PROPERTIES OF REACTION										
$\Delta_r G_m^0$	DGR	3.4	3.4	3.4	3.4	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r H_m^0$	DHR	3.6	3.6	3.6	3.6	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r S_m^0$	DSR	3.8	3.8	3.8	3.8	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r C_{p,m}^0$	D25CPR	3.1	3.1	3.1	3.1 \Rightarrow 0	3.1	3.1	3.1	E	--
$\Delta_r a$: Maier-Kelley	DACPR	3.11	3.11	3.11	3.11 \Rightarrow 0	E	E	E	--	--
$\Delta_r b$: Maier-Kelley	DBCPR	3.12	3.12	3.12 \Rightarrow 0	3.12 \Rightarrow 0	E	E	set to 0	--	--
$\Delta_r c$: Maier-Kelley	DCCPR	3.13	3.13 \Rightarrow 0	3.13 \Rightarrow 0	3.13 \Rightarrow 0	E	set to 0	set to 0	--	--
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f S_m^0$	SF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f C_{p,m}^0$	CP25F	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	--
$\Delta_f a$: Maier-Kelley	CPAF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	--	--
$\Delta_f b$: Maier-Kelley	CPBF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	--	--
$\Delta_f c$: Maier-Kelley	CPCF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	--	--
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
S_m^0	S0									
$C_{p,m}^0$	CP0									

Legend:

- E Data entered
3.4 Calculated using equation (3.4)
3.1 \Rightarrow 0 Calculated to be zero from equation (3.1)
-- Blank: Not entered or insufficient data to calculate

Table 3: continued

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered						
		116d	17	117a	117b	117c	117d	17a
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	--	--	3.19	3.19	3.19	--	--
B Coef. logK(T) expression	BLGK	--	--	3.16	3.16	3.16	--	--
C Coef. logK(T) expression	CLGK	--	--	3.17	3.17	3.17	--	--
D Coef. logK(T) expression	DLGK	--	--	3.15	3.15	3.15	--	--
E Coef. logK(T) expression	ELGK	--	--	3.14	3.14	3.14	--	--
logK(25°C)	LGK25	E	E	E	E	E	E	E
PROPERTIES OF REACTION								
$\Delta_r G_m^0$	DGR	2.1	2.1	2.1	2.1	2.1	2.1	2.1
$\Delta_r H_m^0$	DHR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_r S_m^0$	DSR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.2
$\Delta_r C_{p,m}^0$	D25CPR	E	--	3.1	3.1	3.1	3.1	3.1
Δ_r a: Maier-Kelley	DACPR	--	--	2.3	2.3	2.3	--	--
Δ_r b: Maier-Kelley	DBCPR	--	--	2.3	2.3	2.3	--	--
Δ_r c: Maier-Kelley	DCCPR	--	--	2.3	2.3	2.3	--	--
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.4
$\Delta_f S_m^0$	SF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E see NOTE
$\Delta_f C_{p,m}^0$	CP25F	2.3	--	3.1a	3.1a	3.1a	E	E see NOTE
Δ_f a: Maier-Kelley	CPAF	--	--	E	E	E	--	--
Δ_f b: Maier-Kelley	CPBF	--	--	E	E	set to 0	--	--
Δ_f c: Maier-Kelley	CPCF	--	--	E	set to 0	set to 0	--	--
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
S_m^0	S0							E see NOTE
$C_{p,m}^0$	CP0							E see NOTE

NOTE: Values for $\Delta_f S_m^0$ and $\Delta_f C_{p,m}^0$ (designated SFE and CP25FE) can also be calculated from S_m^0 and $C_{p,m}^0$ data for elements and other entities using equation (2.10) or (2.11). If values for both SF and SFE, and for CP25F and CP25FE are present they are compared. If they differ by more than 0.01, an error message appears on the screen. For case 17a, SFE and possibly CP25FE are available and can be used to enter the missing SF and CP25F.

Table 3: continued

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered			Absolute Entropy (and Absolute Heat Capacity) Entered			
		1 8	1 9	2 0	2 1 a	2 1 b	2 2 a	2 2 b
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	--	--	--	--	--	--	--
B Coef. logK(T) expression	BLGK	--	--	--	--	--	--	--
C Coef. logK(T) expression	CLGK	--	--	--	--	--	--	--
D Coef. logK(T) expression	DLGK	--	--	--	--	--	--	--
E Coef. logK(T) expression	ELGK	--	--	--	--	--	--	--
logK(25°C)	LGK25	E	2.1	2.1	2.1	2.1	2.1	2.1
PROPERTIES OF REACTION								
$\Delta_r G_m^0$	DGR	2.1	E	2.3	2.2	2.2	2.3	2.3
$\Delta_r H_m^0$	DHR	--	--	--	2.3	2.3	2.2	2.2
$\Delta_r S_m^0$	DSR	--	--	--	2.12	2.12	2.12	2.12
$\Delta_r C_{p,m}^0$	D25CPR	--	--	--	--	2.13	--	2.13
$\Delta_r a$: Maier-Kelley	DACPR	--	--	--	--	--	--	--
$\Delta_r b$: Maier-Kelley	DBCPR	--	--	--	--	--	--	--
$\Delta_r c$: Maier-Kelley	DCCPR	--	--	--	--	--	--	--
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	E	2.3	2.3	E	E
$\Delta_f H_m^0$	HF	--	--	--	E	E	2.3	2.3
$\Delta_f S_m^0$	SF	--	--	--	2.4	2.4	2.4	2.4
$\Delta_f C_{p,m}^0$	CP25F	--	--	--	--	2.3	--	2.3
$\Delta_f a$: Maier-Kelley	CPAF	--	--	--	--	--	--	--
$\Delta_f b$: Maier-Kelley	CPBF	--	--	--	--	--	--	--
$\Delta_f c$: Maier-Kelley	CPCF	--	--	--	--	--	--	--
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
S_m^0	S0				E	E	E	E
$C_{p,m}^0$	CP0				--	E	--	E

Table 4: Compromise version of modified PMATCHC calculation cases. Suggested changes with respect to PEARSON et al. (2001) are shaded and suggested changes with respect to the puristic version in Table 3 are set in bold.

Property	PMATCHC Field Name	Properties of Reaction Entered		Properties of Formation Entered		Mixed and Single Value Properties Entered				
		9	10	14	15	16	116d	17	117d	17a
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	--	--	--	--	--	--	--	--	--
C Coef. logK(T) expression	CLGK	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	3.15	--	3.15	--	--	3.15	--	3.15	3.15
E Coef. logK(T) expression	ELGK	--	--	--	--	--	--	--	--	--
logK(25°C)	LGK25	3.2	3.2	3.2	3.2	E	E	E	E	E
PROPERTIES OF REACTION										
$\Delta_r G_m^0$	DGR	E or 2.2	E or 2.2	2.3	2.3	2.1	2.1	2.1	2.1	2.1
$\Delta_r H_m^0$	DHR	E or 2.2	E or 2.2	2.3	2.3	E or 2.2	E or 2.2	2.3	2.3	2.3
$\Delta_r S_m^0$	DSR	E or 2.2	E or 2.2	2.3	2.3	E or 2.2	E or 2.2	2.3	2.3	2.2
$\Delta_r C_{p,m}^0$	D25CPR	E	--	3.1	--	--	E	--	3.1	3.1
$\Delta_r a$: Maier-Kelley	DACPR	--	--	--	--	--	--	--	--	--
$\Delta_r b$: Maier-Kelley	DBCPR	--	--	--	--	--	--	--	--	--
$\Delta_r c$: Maier-Kelley	DCCPR	--	--	--	--	--	--	--	--	--
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	2.3	2.3	E or 2.4	E or 2.4	2.3	2.3	E or 2.4	E or 2.4	2.4
$\Delta_f S_m^0$	SF	2.3	2.3	E or 2.4	E or 2.4	2.3	2.3	E or 2.4	E or 2.4	E see NOTE
$\Delta_f C_{p,m}^0$	CP25F	2.3	--	E	--	--	2.3	--	E	E see NOTE
$\Delta_f a$: Maier-Kelley	CPAF	--	--	--	--	--	--	--	--	--
$\Delta_f b$: Maier-Kelley	CPBF	--	--	--	--	--	--	--	--	--
$\Delta_f c$: Maier-Kelley	CPCF	--	--	--	--	--	--	--	--	--
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
S_m^0	S0									E see NOTE
$C_{p,m}^0$	CP0									E see NOTE

Legend:

E	Data entered
3.4	Calculated using equation (3.4)
3.1 \Rightarrow 0	Calculated to be zero from equation (3.1)
--	Blank: Not entered or insufficient data to calculate
NOTE	See facing page

Table 4: continued

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered			Absolute Entropy (and Absolute Heat Capacity) Entered			
		18	19	20	21a	21b	22a	22b
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	set to logK (25 °C)	set to logK (25 °C)	set to logK (25 °C)	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	--	--	--	--	--	--	--
C Coef. logK(T) expression	CLGK	--	--	--	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	--	--	--	--	3.15	--	3.15
E Coef. logK(T) expression	ELGK	--	--	--	--	--	--	--
logK(25°C)	LGK25	E	2.1	2.1	3.2	3.2	3.2	3.2
PROPERTIES OF REACTION								
$\Delta_r G_m^0$	DGR	2.1	E	2.3	2.2	2.2	2.3	2.3
$\Delta_r H_m^0$	DHR	--	--	--	2.3	2.3	2.2	2.2
$\Delta_r S_m^0$	DSR	--	--	--	2.12	2.12	2.12	2.12
$\Delta_r C_{p,m}^0$	D25CPR	--	--	--	--	2.13	--	2.13
$\Delta_r a$: Maier-Kelley	DACPR	--	--	--	--	--	--	--
$\Delta_r b$: Maier-Kelley	DBCPR	--	--	--	--	--	--	--
$\Delta_r c$: Maier-Kelley	DCCPR	--	--	--	--	--	--	--
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	E	2.3	2.3	E	E
$\Delta_f H_m^0$	HF	--	--	--	E	E	2.3	2.3
$\Delta_f S_m^0$	SF	--	--	--	2.4	2.4	2.4	2.4
$\Delta_f C_{p,m}^0$	CP25F	--	--	--	--	2.3	--	2.3
$\Delta_f a$: Maier-Kelley	CPAF	--	--	--	--	--	--	--
$\Delta_f b$: Maier-Kelley	CPBF	--	--	--	--	--	--	--
$\Delta_f c$: Maier-Kelley	CPCF	--	--	--	--	--	--	--
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
S_m^0	S0				E	E	E	E
$C_{p,m}^0$	CP0				--	E	--	E

NOTE: Values for $\Delta_f S_m^0$ and $\Delta_f C_{p,m}^0$ (designated SFE and CP25FE) can also be calculated from S_m^0 and $C_{p,m}^0$ data for elements and other entities using equation (2.10) or (2.11). If values for both SF and SFE, and for CP25F and CP25FE are present they are compared. If they differ by more than 0.01, an error message appears on the screen. For case 17a, SFE and possibly CP25FE are available and can be used to enter the missing SF and CP25F.

APPENDIX: EQUATIONS USED FOR CALCULATION OF NON-ENTERED DATA

Equation numbers refer to PEARSON et al. (2001).

$$\Delta_r G_m^\circ = -R \cdot T^\circ \cdot \ln(10) \cdot \log K^\circ \quad (2.1)$$

$$\Delta_r G_m^\circ = \Delta_r H_m^\circ - T^\circ \cdot \Delta_r S_m^\circ \quad (2.2)$$

$$\Delta_r X_m^\circ = \Sigma \Delta_f X_m^\circ(\text{products}) - \Sigma \Delta_f X_m^\circ(\text{reactants}) \quad (2.3)$$

$$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T^\circ \cdot \Delta_f S_m^\circ \quad (2.4)$$

$$\Delta_r S_m^\circ = \Sigma S_m^\circ(\text{products}) - \Sigma S_m^\circ(\text{reactants}) \quad (2.12)$$

$$\Delta_r C_{p,m}^\circ = \Sigma C_{p,m}^\circ(\text{products}) - \Sigma C_{p,m}^\circ(\text{reactants}) \quad (2.13)$$

$$\Delta_r C_{p,m}^\circ(T) = \Delta_r a + \Delta_r b \cdot T - \Delta_r c / T^2 \quad (3.1)$$

$$\Delta_f C_{p,m}^\circ(T) = \Delta_f a + \Delta_f b \cdot T - \Delta_f c / T^2 \quad (3.1a)$$

$$\log K^\circ(T) = A + B \cdot T + C / T + D \cdot \log(T) + E / T^2 \quad (3.2)$$

$$\Delta_r G_m^\circ(T) = -R \cdot \ln(10) \cdot (A \cdot T + B \cdot T^2 + C + D \cdot T \cdot \log(T) + E / T) \quad (3.4)$$

$$\Delta_r H_m^\circ(T) = R \cdot \ln(10) \cdot (B \cdot T^2 - C + D \cdot T / \ln(10) - 2 \cdot E / T) \quad (3.6)$$

$$\Delta_r S_m^\circ(T) = R \cdot \ln(10) \cdot (A + 2 \cdot B \cdot T + D / \ln(10) \cdot (1 + \ln(T)) - E / T^2) \quad (3.8)$$

$$\Delta_r a = R \cdot D \quad (3.11)$$

$$\Delta_r b = 2 \cdot R \cdot \ln(10) \cdot B \quad (3.12)$$

$$\Delta_r c = -2 \cdot R \cdot \ln(10) \cdot E \quad (3.13)$$

$$E = -\Delta_r c / (2 \cdot R \cdot \ln(10)) \quad (3.14)$$

$$D = \Delta_r a / R \quad (3.15)$$

$$B = \Delta_r b / (2 \cdot R \cdot \ln(10)) \quad (3.16)$$

$$C = B \cdot T^{\circ 2} + D \cdot T^\circ / \ln(10) - 2 \cdot E / T^\circ - \Delta_r H_m^\circ(T^\circ) / (R \cdot \ln(10)) \quad (3.17)$$

$$A = \Delta_r S_m^\circ(T^\circ) / (R \cdot \ln(10)) - 2 \cdot B \cdot T^\circ - D / \ln(10) \cdot (1 + \ln(T^\circ)) + E / T^{\circ 2} \quad (3.19)$$