**Part 1. Temperature corrections of standard molar thermodynamic properties of condensed substances and gases using data in DComp records of GEM-Selektor**

This calculation is derived from integration of the heat capacity equation *Cp* = *f*(*T*) which has the following form:

** (1-1)

where *ai* are the empirical coefficients, and power coefficients *ni* are: *n*0 = 0; *n*1 = 1; *n*2 = -2; *n*3 = -0.5; *n*4 = 2; *n*5 = 3; *n*6 = 4; *n*7 = -3; *n*8 = -1; *n*9 = 0.5. Some of these terms are used in most published databases. The corresponding isobaric heat capacity equation is:

*Cp* = *a0*  + *a1T*  +  *a2 T* -2  + *a3 T* -0.5 +  *a4 T* 2  + *a5 T* 3 + (1-2).

         + *a6 T* 4 + *a7 T* -3  + *a8 T* -1  + *a9 T* 0.5.

As known from chemical thermodynamics (e.g., Anderson and Crerar, 1993), the increment of standard molar Gibbs energy *Go* at the reference pressure *Pr* = 1 bar from reference temperature *Tr* to temperature of interest *T* (in K) can be found by integrating the absolute molar entropy *So* :

 (1-3),

where . Equation (1-3) can be transformed as follows:

 (1-4),

where the terms stand for the Temkin-Shwarzman functions of temperature (Dorogokupets et al., 1988):

.

Using these functions and coefficients *ni* from eqn. (1-1), separate terms can be defined:







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Now, the standard molar apparent Gibbs energy function *goT* of a substance can be calculated easily at reference pressure *Pr* = 1 bar and temperature of interest *T* ≠ *Tr* (usually, reference temperature *Tr* = 298.15 K):

 (1-5)

In a similar way, the standard molar entropy  at *Pr* and *T* can be calculated

 (1-6),

as well as the standard molar apparent enthalpy function :

 (1-7)

For any compound substance, the apparent molar  and  can be converted into standard molar Gibbs energy  and enthalpy  of formation from elements, respectively:

; (1-8)

. (1-9)

It follows that at *Tr* =298.15 K,  and  because, for any element at its standard state,  and  by convention. Note that in Selektor codes (as well as in SUPCRT92; Johnson et al., 1992), apparent molar functions  and , but not the formation functions  and  are calculated throughout at elevated temperatures.

It is possible that, within a wide temperature range, the heat capacity function *Cp* = *f*(*T*) is approximated by more than one set of coefficients of the form eqns (1-1) and (1-2). In the DComp data format, up to 10 such sets are allowed, and each set of coefficients must be supplied with a temperature applicability interval [*Tmin*; *Tmax*]. No break is allowed within the whole temperature range covered by *n*(*Q*) sets; i.e. .

For simplicity, let *T*0 be the lowest temperature for the first *Cp* approximation interval; *T*1 be the upper temperature for the latter (*T*0 to *T*1) and at the same time – the lower boundary for the next interval (*T*1 to *T*2), and so on. Usually, *T*0 equals 273.15 or 298.15 K, and some of the intermediate temperature boundaries refer also to temperatures of phase transitions at *P* = *Pr*.

Let *k* be the index of the temperature interval containing the temperature of interest *Tint.* Obviously, if *k* = 0 and *T*0 ≤ *Tr* < *T*1 then *T*0 ≤ *Tint* ≤ *T*1 and eqns (1-2) and (1-5) to (1-7) apply directly using the first set of *Cp*=*f*(*T*) coefficients. If *k* > *0* then the value of molar *Cp* at *T* = *Tint* where *Tk* ≤ *Tint* ≤ *Tk*+1 is still found from eqn (1-2) applied directly to the *k*-th set of *Cp* coefficients. However, the values of  ,  and must be calculated incrementally in *k* loops, as shown in the flow chart below, which also includes accounting for optional molar increments *S*FT, *H*FT, *G*FT at phase transitions. It is required that the temperature of any phase transition *TFT* (at *Pr*) always co-insides with one of the boundary temperatures *Tj*+1.

Initial: Set *j* = 0; *Tr* = 298.15 K and *T* = *Tj*+1 ;

Set *Tr* = *Tj*+1;  *j* = *j* +1; and *T* = min(*Tj*+1,*Tint*)

Compute

 (eqn 1-5),

 (eqn 1-6),

 (eqn 1-7)

Check if *j* < *k*

yes

no

Calculate *CpT* (eqn 1-2); Final , , , *CpT*

Is there a phase transition

at *T*FT = *Tj*+1?

Set  ; 

Retrieve non-zero *S*FT, *H*FT, and *G*FT

yes

no

Set zero *S*FT, *H*FT, and *G*FT

Note that usage of GEM solvers of equilibria does not really require representing phase transitions in a single DComp record as for a single dependent component. Polymorph modifications, as well as solid, liquid and gaseous states of a substance can be represented as different phases or phase components (i.e. separate DComp records), because GEM will always select the most stable one at *T,P* of interest. Besides, this also allows circumventing the problem of pressure dependence of the phase transition temperature.

**References**

Anderson G.M., Crerar D.A. (1993) *Thermodynamics in geochemistry: The equilibrium model.* Oxford Univ. Press, N.Y.,Oxford.

Dorogokupets P.I., Karpov I.K., Lashkevich V.V., Naigebauer V.A., Kazmin L.A. (1988) Isobaric-isothermal potentials of minerals, gases and aqueous species in the “Selektor” program package. In: *Physicochemical models in geochemistry* (Kiselev A.I., Karpov I.K., eds.), Nauka Publ., Novosibirsk, p. 124-147 (in Russian).

Johnson J.W., Oelkers E., Helgeson H.C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 oC. *Comp. Geosci.,* **18**, 899-947.

**Appendix 1.1.** Built-in options for calculation of temperature and pressure correction to standard molar (partial molal) properties of condensed substances and fluids (gases) using data in DComp records (GEM-Selektor v. 3.0).

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| Code | Model | Input parameters |
| **CSC** | integration of heat capacity, constant molar volume | empirical *Cp* coefficients (*a0* to *a*9) entered into **aiCpT** array; optional phase transition parameters entered into **FT\_p** array |
| **CSK** | integration of heat capacity, molar volume from empirical *V* = *f*(*T*,*P*) function | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; 5 empirical coefficients for molar volume (*a0*, *a1*, *a3*, *b0*, *b1*) entered into **aiVTP** array; optional phase transition parameters entered into **FT\_p** array |
| **CSE** | integration of heat capacity, molar volume from HP Birch-Murnaghan equation | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; isothermal compressibility and isobaric expansibility into **BetAlp** fields |
| **CHE** | integration of heat capacity with Landau contribution, molar volume from HP Birch-Murnaghan equation | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; isothermal compressibility and isobaric expansibility into **BetAlp** fields; *Smax* and *Tcrit* of Lambda transition into **LamST** fields; *Vmax* into **ab[0]** field |
| **CSB** | integration of heat capacity, molar volume from Birch-Murnaghan equation | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; coefficients of BM equation into **ai0Dc** array |
| **CSS** | integration of ideal gas heat capacity, *VdP* contribution from Churakov-Gottschalk (CG) fluid EoS | empirical *Cp* coefficients (*a*0 to *a*9)entered into **aiCpT** array; coefficients of CG fluid EoS (*sig*, *eps*, *mu*, *alp*) into **Cemp\_s** array |
| **CSR** | integration of ideal gas heat capacity, *VdP* contribution from Peng-Robinson-Stryjek-Vera (PRSV) fluid EoS | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; coefficients of PRSV fluid EoS (*Tc*, *Pc*, *ω*, *k1*, *k2*, *k3*) into **CritPg** array |
| **CS7** | integration of ideal gas heat capacity, *VdP* contribution from Peng-Robinson (PR78) fluid EoS | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; coefficients of PR78 fluid EoS (*Tc*, *Pc*, *ω*) into **CritPg** array |
| **CS8** | integration of ideal gas heat capacity, *VdP* contribution from compensated Redlich-Kwong (CORK) fluid EoS | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; coefficients of CORK fluid EoS (*Tc*, *Pc*) into **CritPg** array; for H2O and CO2 special built-in routines are used that are activated through the DComp species codes V (H2O) and C (CO2) |
| **CST** | integration of ideal gas heat capacity, *VdP* contribution from Soave-Redlich-Kwong (SRK) fluid EoS | empirical *Cp* coefficients (*a*0 to *a*9) entered into **aiCpT** array; coefficients of SRK fluid EoS (*Tc*, *Pc*, *ω*) into **CritPg** array |

**Appendix 1.2.** Built-in options for calculation of temperature and pressure correction to standard molar (partial molal) properties of aqueous species (and water) using data in DComp records (GEM-Selektor v. 3.0).

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| Code | Model | Input parameters |
| **CSA** | integration of heat capacity, hydration properties of aqueous species from the Akinfiev-Diamond nonelectrolyte model | empirical Cp coefficients (*a0* to *a9*) entered into **aiCpT** array; 3 coefficients of the Akinfiev-Diamond nonelectrolyte model (*xi*, *a*, *b*) into **aiNEs** array |
| **HWF** | water properties (stable state in single-phase fields, liquid properties on two-phase curve) from Haar-Gallagher-Kell (HGK) model | only standard state data need to be provided; paramters of HKF model in **aiHKF** array are all set to zero |
| **HWG** | properties of water vapor (on two-phase curve) from Haar-Gallagher-Kell (HGK) model | only standard state data need to be provided; paramters of HKF model in **aiHKF** array are all set to zero |
| **HKF** | aqueous species properties from revised Helgeson-Kirkham-Flowers (HKF) model | coefficients of revised HKF model (*a1*, *a2*, *a3*, *a4*, *c1*, *c2*, *ω0*) into **aiHKF** array (in their original calorie-based units) |
| **HKP** | prediction of HKF parameters of aqueous complexes using Parcor correlation algorithm | DComp record is automatically created from ReacDC calculation in PRONSPREP/Parcor mode. Only recalculation of DComp is required to obtain correct standard state properties. Upon this, the code will be automatically changed to **HKF**. |