



Aalto University

CHEM-E6100

Fundamentals of chemical thermodynamics

Week 3, Fall 2021

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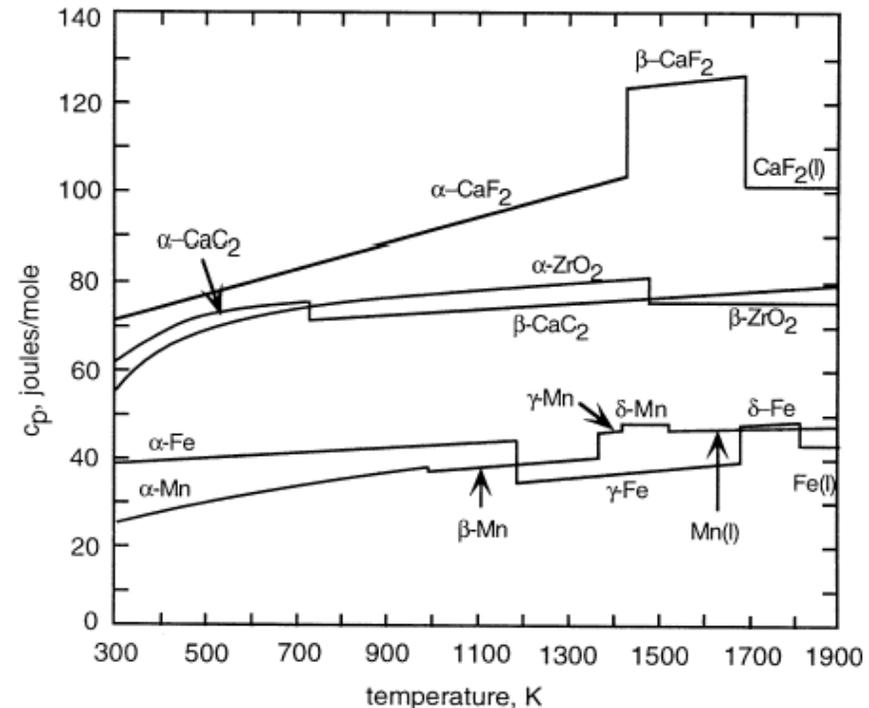
- **Heat capacity (Ch. 6)**
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Heat capacity - Specific heat

- Two different specific heat functions; the property of a substance in constant volume and constant pressure
$$C_v = (\partial U / \partial T)_v$$
$$C_p = (\partial H / \partial T)_p.$$
- Their equations can also be written as
$$dU = C_v dT$$
$$dH = C_p dT.$$
- In processes under constant pressure $(P, T_1) \rightarrow (P, T_2)$ the integral form of the difference of system enthalpy is
$$\Delta H = H(P, T_2) - H(P, T_1) = \int_{T_1}^{T_2} C_p dT.$$

Specific heat

- The enthalpy difference or 'heat content' of a system is obtained by integrating its specific heat C_p over the temperature interval $T_1 \rightarrow T_2$
- If we are interested in thermal effects of substances and systems we need to know C_p (or c_p) as a function of temperature for each substance of the system.



Modelling the specific heat

- Specific heat of a substance has been modelled by quantum theoretical assumptions with limited success.
- They were preceded by
 - Dulong-Petit 'law' (1819); it states that all solid substances have specific heat in constant volume about $c_v=3R$, and
 - Kopp's (1865) 'rule' (Neumann-Kopp rule); it states that the specific heat c_v of intermetallic compounds is sum of their metal components weighed by their molar fractions.
- Einstein (1907) treated the problem using quantum mechanics and again Debye (1912).

Specific heat at low temperatures

- According to Debye, a 'theoretical' model of specific heat is given by equation

$$c_v = 9R(T/\theta_D)^3 \int_0^{\theta_D/T} x^4 e^{-x}/(1-e^{-x}) dx.$$

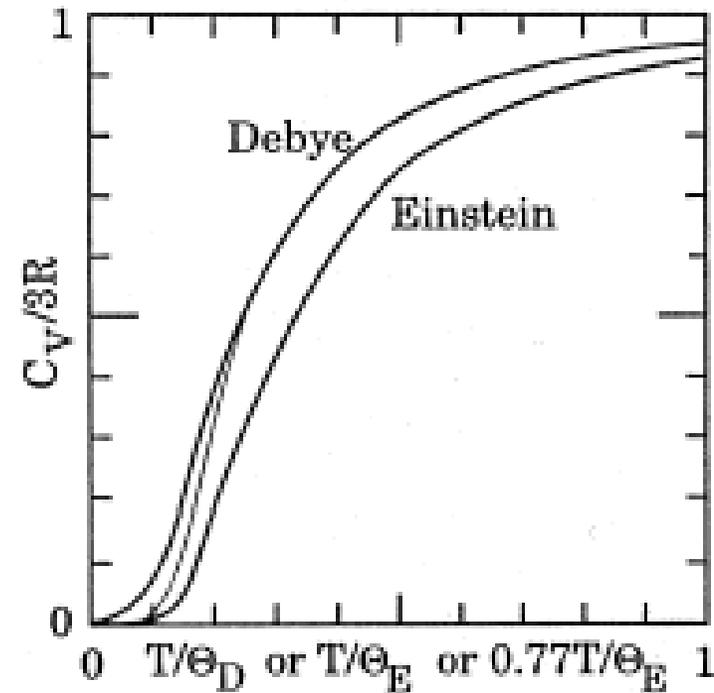
where θ_D is characteristic Debye temperature of the substance and the variable $x = hv/(kT)$, where ν is vibrational frequency of the substance, h is Planck constant and k Boltzmann constant.

Specific heat at low temperatures

- The value of integral from zero to infinite is 25.98; thus at very low temperature we get

$$c_v = 9R \times 25.98 (T/\theta_D)^3,$$

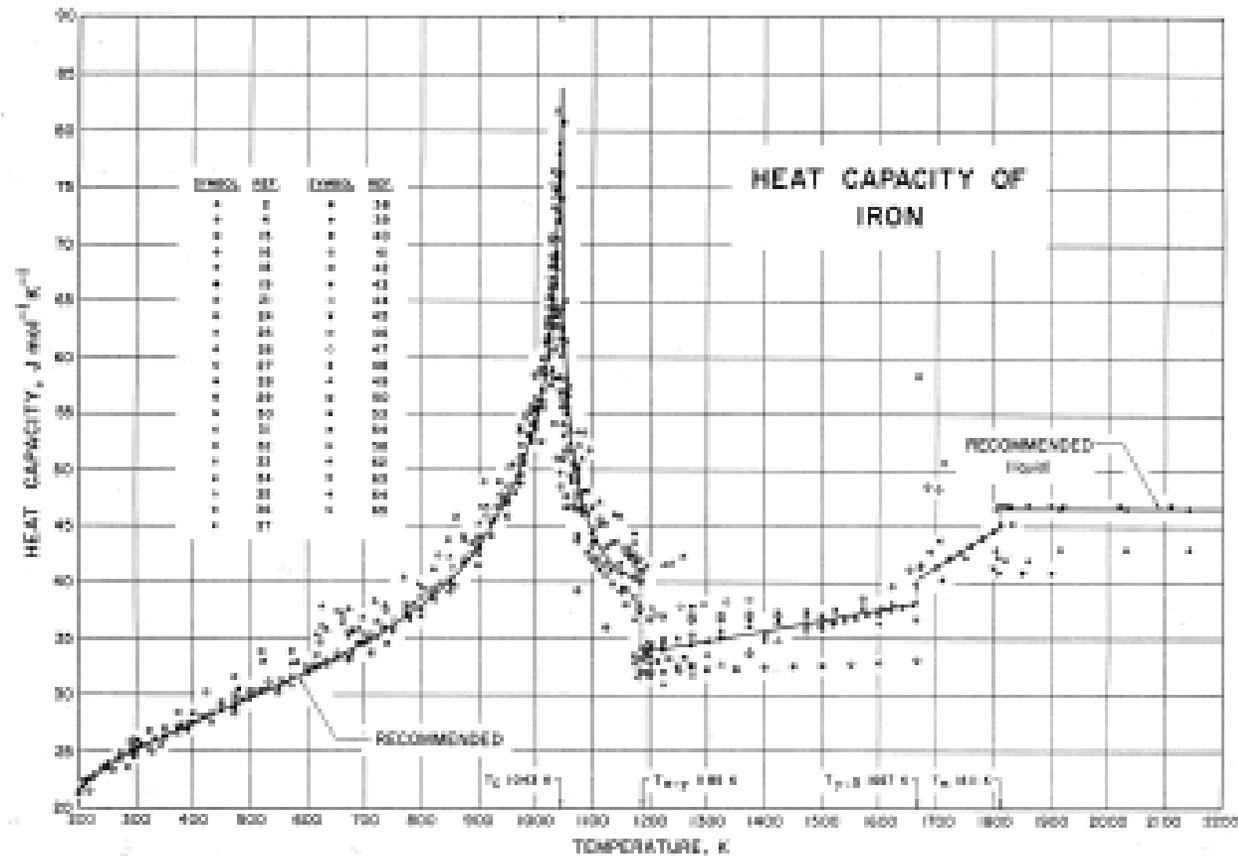
- known as Debye's T^3 law.
- It is used for fitting c_v with experimental values at low temperatures.



Specific heat in technical applications

- All industrial manufacturing processes operate above room temperature.
- Therefore, it is important from application point of view how c_p (or c_v) can be modelled above 25 °C.
- The practical models are based on the phenomena or are phenomenological.
- The temperature plot of specific heat has discontinuities at structural transformations, e.g.
 - melting.
 - transformation in crystal structure.
 - magnetic transformation/ordering.
 - chemical ordering.

Specific heat in technical applications



Kelley equation

- Analytical forms of the state functions are (generally) unknown
- Specific heat (of a substance) is fitted from experimental data using polynomial series
- The most common is the Kelley equation, which has the form:

$$C_p = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2 \text{ (originally '- c} \cdot T^{-2}\text{')}$$

- Where a, b, c, and d are parameters fitted from experimental data

Kelley equation

- The Kelley equation is often fitted with different parameters, stepwise in different temperature ranges
- A problem of this approach is the metastable regions – this is particularly important in material sciences
- We need either theoretical models or rational agreements on how $c(T,P)$ will be extrapolated to areas without experimental observations

Temperature dependency of enthalpy

- In a closed system, in isobaric processes at constant composition $T_1 \rightarrow T_2$ change of enthalpy can be written as

$$\Delta H = H(P, T_2) - H(P, T_1) = \int_{T_1}^{T_2} C_p \, dT.$$

- Thus ΔH is the area between c_p function value and abscissa axis over the temperature interval $T_1 - T_2$.
- The changes (or 'processes') where $\Delta H > 0$ are called endothermic (a 'reaction' requiring heat)
- And $\Delta H < 0$ are called exothermic (releasing heat).

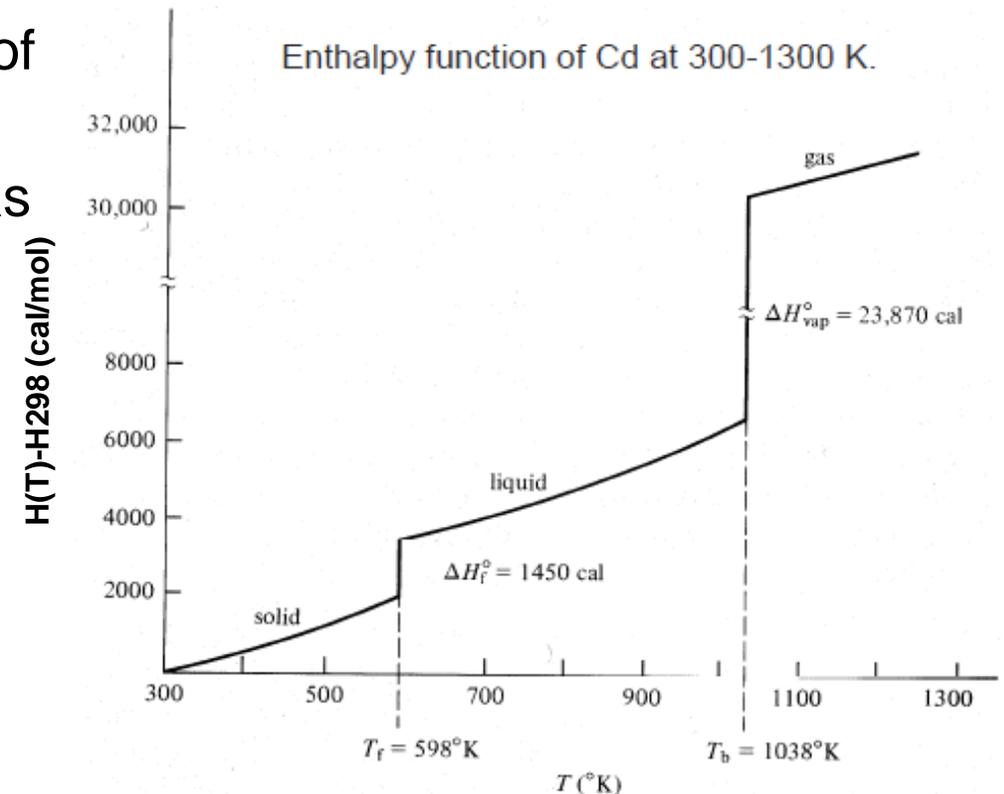
Temperature dependence of Enthalpy

- It was shown previously that the integral form of c_p -function with respect of temperature is the change of system enthalpy in isobaric conditions.
- This definition gives enthalpy its general equation as a function of temperature

$$H(P,T) = {}^\circ H(P, 298.15) + \int_{298.15}^T c(\alpha)_p dT + \Delta H(\alpha) + \dots + \int_{T_0}^T c(2)_p dT$$

where $\Delta H(\alpha)$ are *phase transformation enthalpies* within the interval 298.15-T.

- **Enthalpy is thus *discontinuous* at every transformation temperature.**



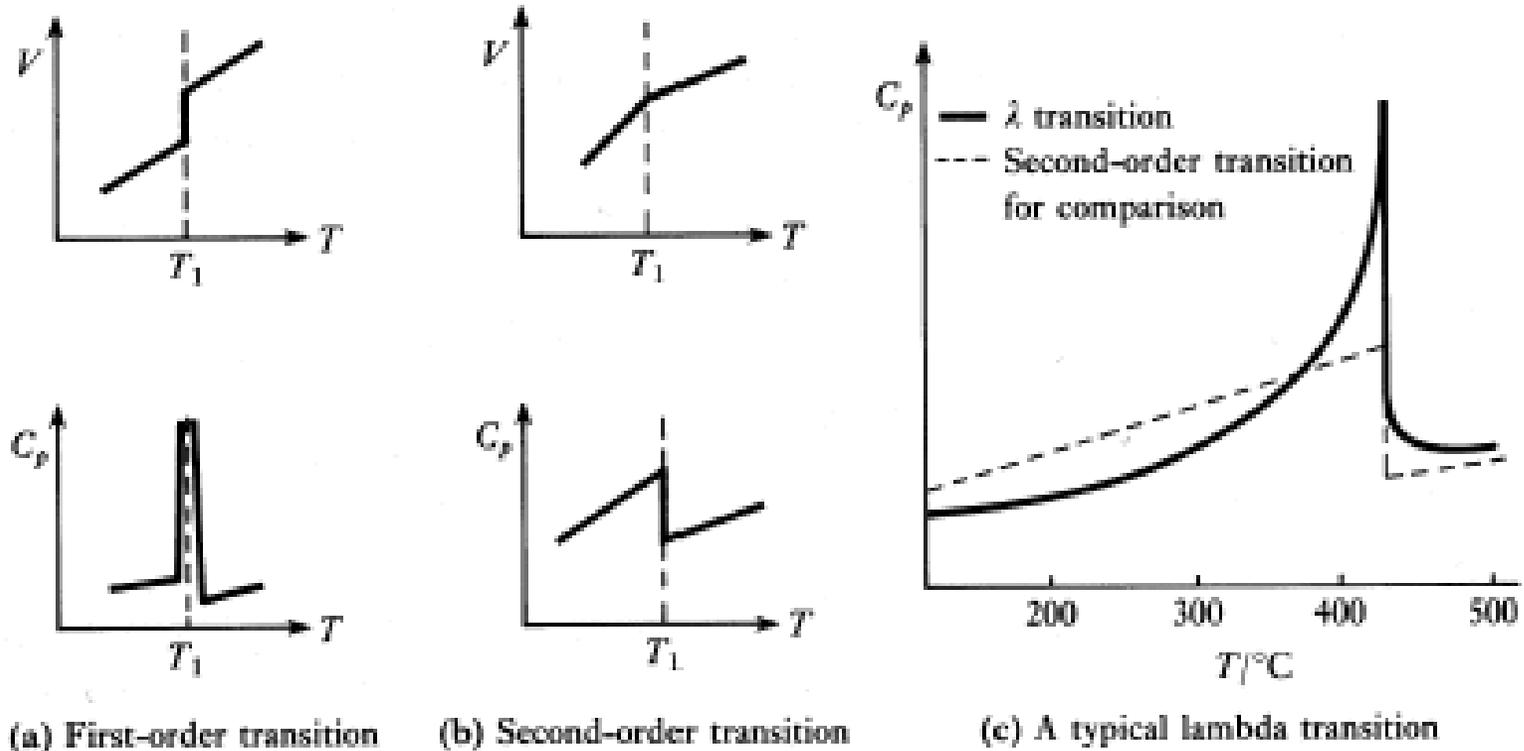
Enthalpy of substances

- Thus
$$\begin{aligned}\Delta H(T) &= H(P,T) - H(P,298.15) \\ &= \int_{298}^T c_p \, dT \\ &= \int_{298}^{T^\alpha} c(\alpha)_p \, dT + \Delta H(\alpha) + \dots + \int_{T^\delta}^T c(2)_p \, dT .\end{aligned}$$
- The $c(\alpha)_p$ is the c_p function of each temperature range α and $\Delta H(\alpha)$ is the related enthalpy of phase transformation.

Heat of phase transformation

- All structural transformations can be 'seen' in the c_p function and as a result, also in the other state functions of substances (through Maxwell relations).
- Some cause a point of discontinuity and the others change its slope ($\partial c_p / \partial T$).

Heat of phase transformation



Various phase transformations: 1st order transformation is connected with volume difference, 2nd order not.

Heat of phase transformation

- **First-order phase transitions are those that involve a latent heat.**
- **A system either absorbs or releases a fixed amount of energy per volume.**
- **During this process, the temperature of the system will stay constant as heat is added as some parts of the system have completed the transition and others have not.**
- **Examples are melting and boiling.**

Heat of phase transformation

- **Second-order phase transitions are characterized by a divergent susceptibility, an infinite correlation length, and a power-law decay of correlations near criticality.**
- **Examples are ferromagnetic transition, superconducting transition and superfluid transition.**
- **Lambda transitions are for example solid state phase transitions.**

Heat of phase transformation

- For pure substances phase transformations are seen as discontinuities where at (phase transformation) temperature T_{tr} occurs a (spontaneous) reaction



- In that process, enthalpy change is

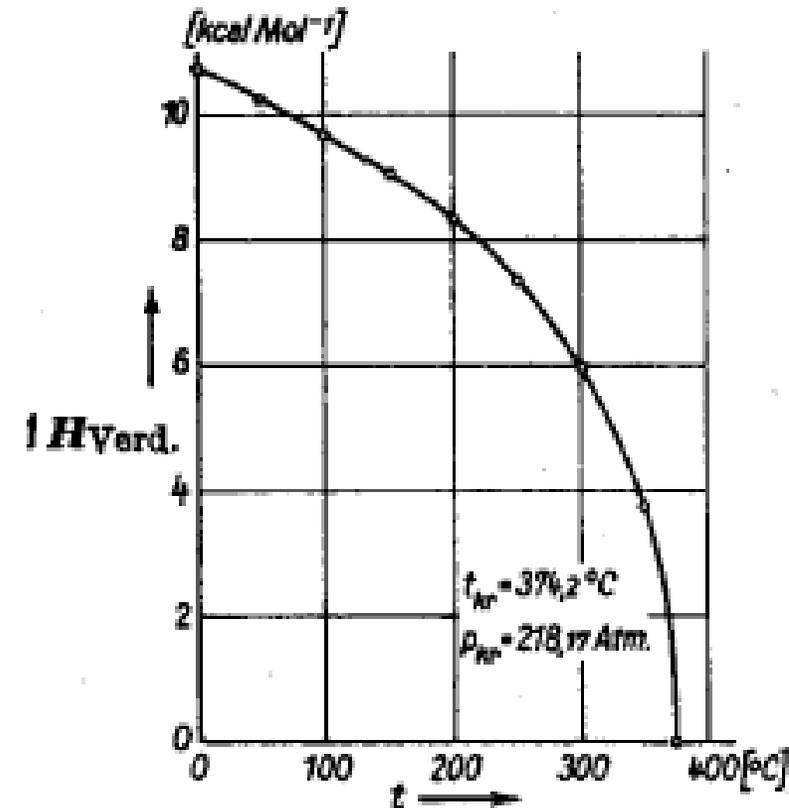
$$\Delta H(T_{tr}) = H[A_{(2)}] - H[A_{(1)}]$$

where $H[A_{(1)}]$ and $H[A_{(2)}]$ are enthalpies of phases 1 and 2 at phase transformation temperature T_{tr}

- It is called the heat or enthalpy of phase transformation.

Heat of phase transformation

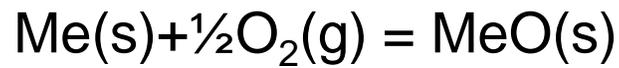
- Enthalpy of phase transformation is not constant or independent of temperature, but its value depends on the c_p functions and their pressure and temperature relations.



Standard enthalpy of a compound

Enthalpy of (pure) substances tells nothing about standard enthalpy of compounds and their enthalpy of formation. As stated earlier, the change of enthalpy when a compound is formed is $\Delta H = \{\text{product}\} - \{\text{reactant}\}$.

- When an oxide is formed from pure elements we can e.g. write



and its thus standard heat or enthalpy of reaction is *by definition*

$$\Delta H = {}^\circ H_{\text{MeO(s)}} - {}^\circ H_{\text{Me(s)}} - \frac{1}{2} {}^\circ H_{\text{O}_2(\text{g})}.$$

- At reference temperature 298.15 K and 1 bar pressure the enthalpies of pure elements Me(s) and O₂(g) are zero; the above equation simplifies to

$$\Delta H = {}^\circ H_{\text{MeO(s)}}.$$

In general: the standard enthalpy of a compound is equal to its enthalpy of formation at 25 °C when it forms from pure elements (in their reference states).

Temperature dependence of heat of reaction

- Enthalpies of the reactants and products at temperature T were obtained in equations

$$H(\text{Me}) = {}^\circ H(\text{Me}) + {}_{298} \int^T c_p(\text{Me})_p dT$$

$$H(\text{O}_2(\text{g})) = {}^\circ H(\text{O}_2(\text{g})) + {}_{298} \int^T c_p(\text{O}_2(\text{g}))_p dT$$

$$H(\text{MeO}) = {}^\circ H(\text{MeO}) + {}_{298} \int^T c_p(\text{MeO})_p dT.$$

- We can write the general equation for enthalpy at any temperature, and get its temperature dependency as

$$\Delta H = H_{\text{MeO}(\text{s})} - H_{\text{Me}(\text{s})} - \frac{1}{2} H_{\text{O}_2(\text{g})}$$

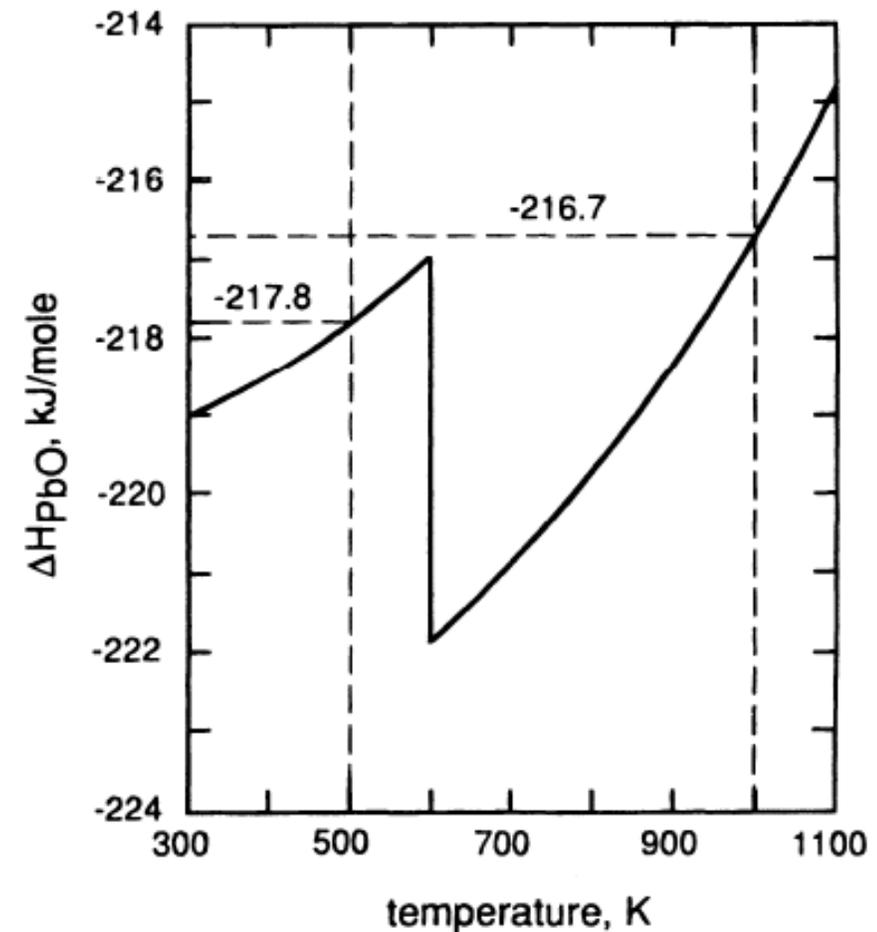
and

$$\Delta H = \Delta H^\circ(\text{MeO}) + {}_{298} \int^T \Delta c_p(\text{MeO})_p dT$$

where $\Delta c_p(\text{MeO})$ is difference of c_p functions between product and the reactants, weighed by the stoichiometric coefficients, and $\Delta H^\circ(\text{MeO})$ is standard enthalpy of formation of the compound.

Example

- In case of enthalpy of formation of lead oxide, the integration has been done in the next plot over the temperature interval of 300-1100 K
- One can see that the **enthalpy of formation has small temperature dependence** (even if the temperature range is wide extending from 300 to 1100 K):
 - and it is only about ± 2 kJ/mol when the order of magnitude of enthalpy is 220 kJ/mol,
 - this means less than 1% around its average value over that temperature interval



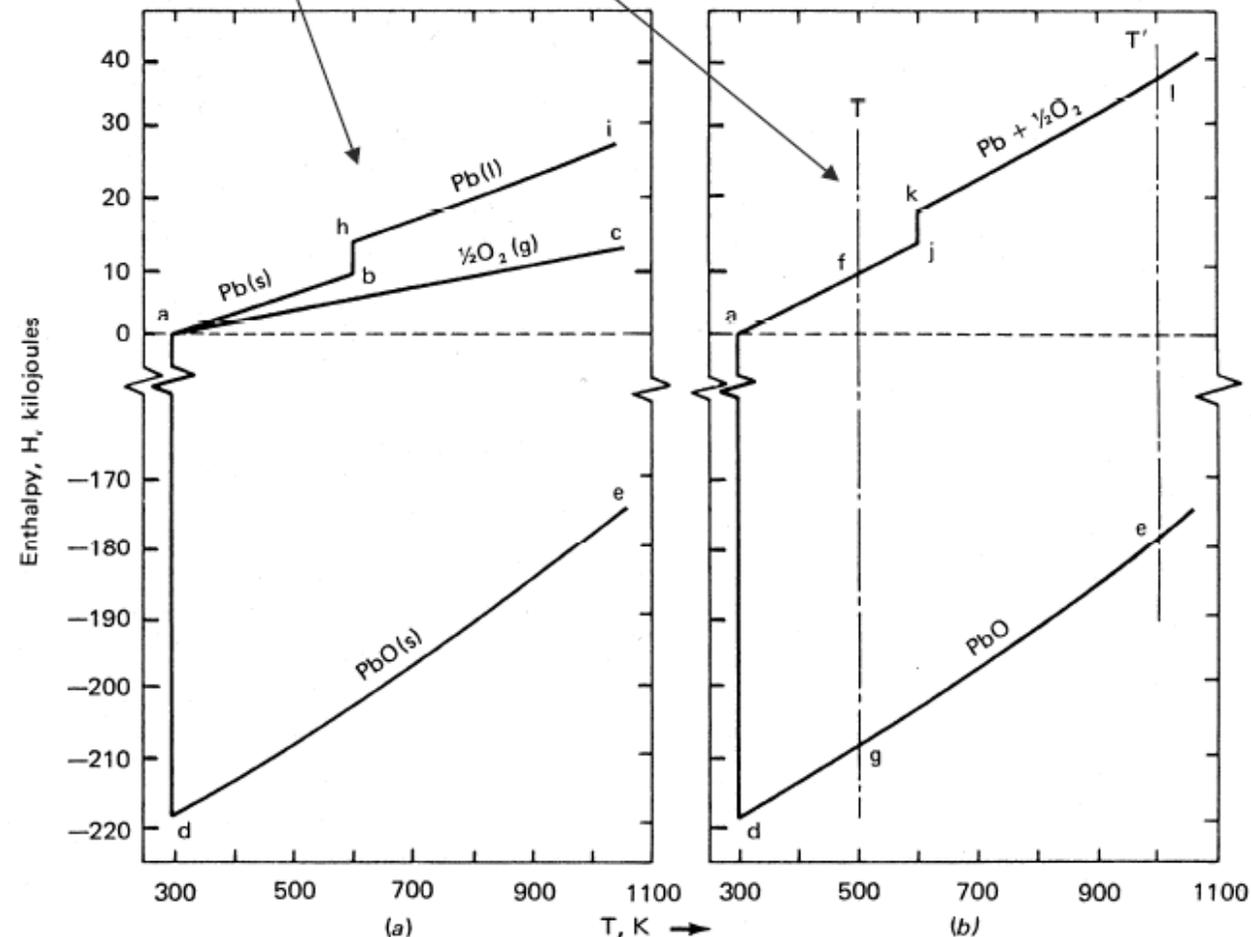
Compounds: temperature dependency of enthalpy

- If we know the standard value of the enthalpy of a compound, its enthalpy at other temperatures can be calculated using the temperature integral of its heat capacity over interval $298.15 - T(K)$.
- Therefore, the **enthalpy plot of a compound does not show the same phase transformations as its component elements.**

Compounds: temperature dependency of enthalpy

- The distance $f-g$ is = the reaction enthalpy at T when the compound is formed from its elements, or it is **the enthalpy of formation**.

Raw materials: separately and their additive plot

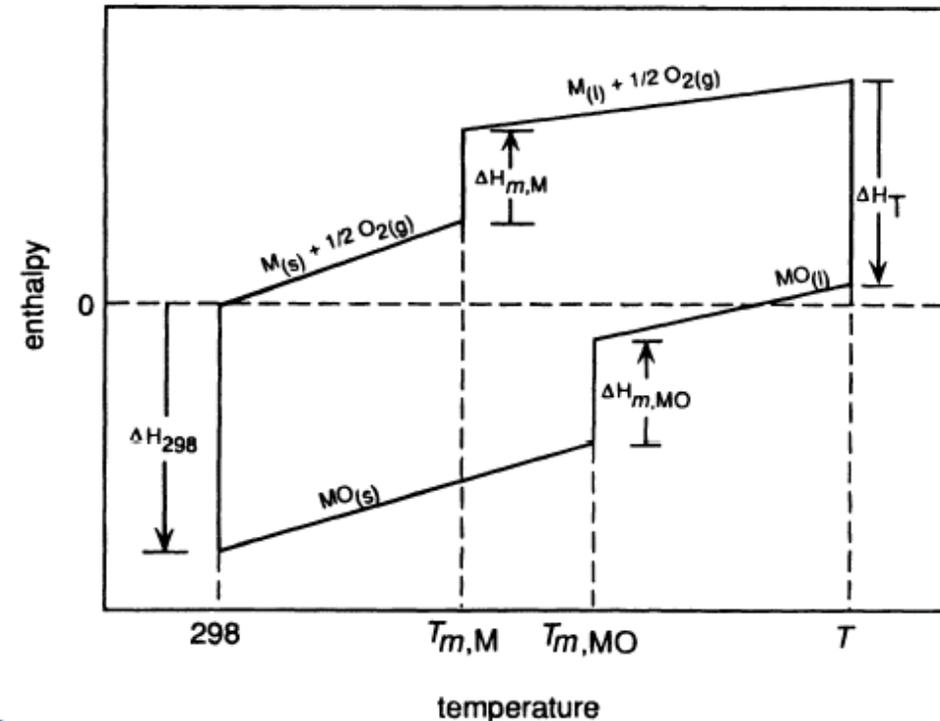


Kirchhoff's law

- Because **enthalpy is a function of state**, its integration in case of a reaction can be made along whatever path.

the change of H can be calculated:

- either by taking into account heat of reaction at room temperature and heating up the products to the final temperature or
- by heating up the raw materials to the final temperature of reaction and calculating the heat of reaction at that temperature.



Because of this, process calculations are often made at room temperature and the overall heat balance is calculated through the energy needed for heating up the products.

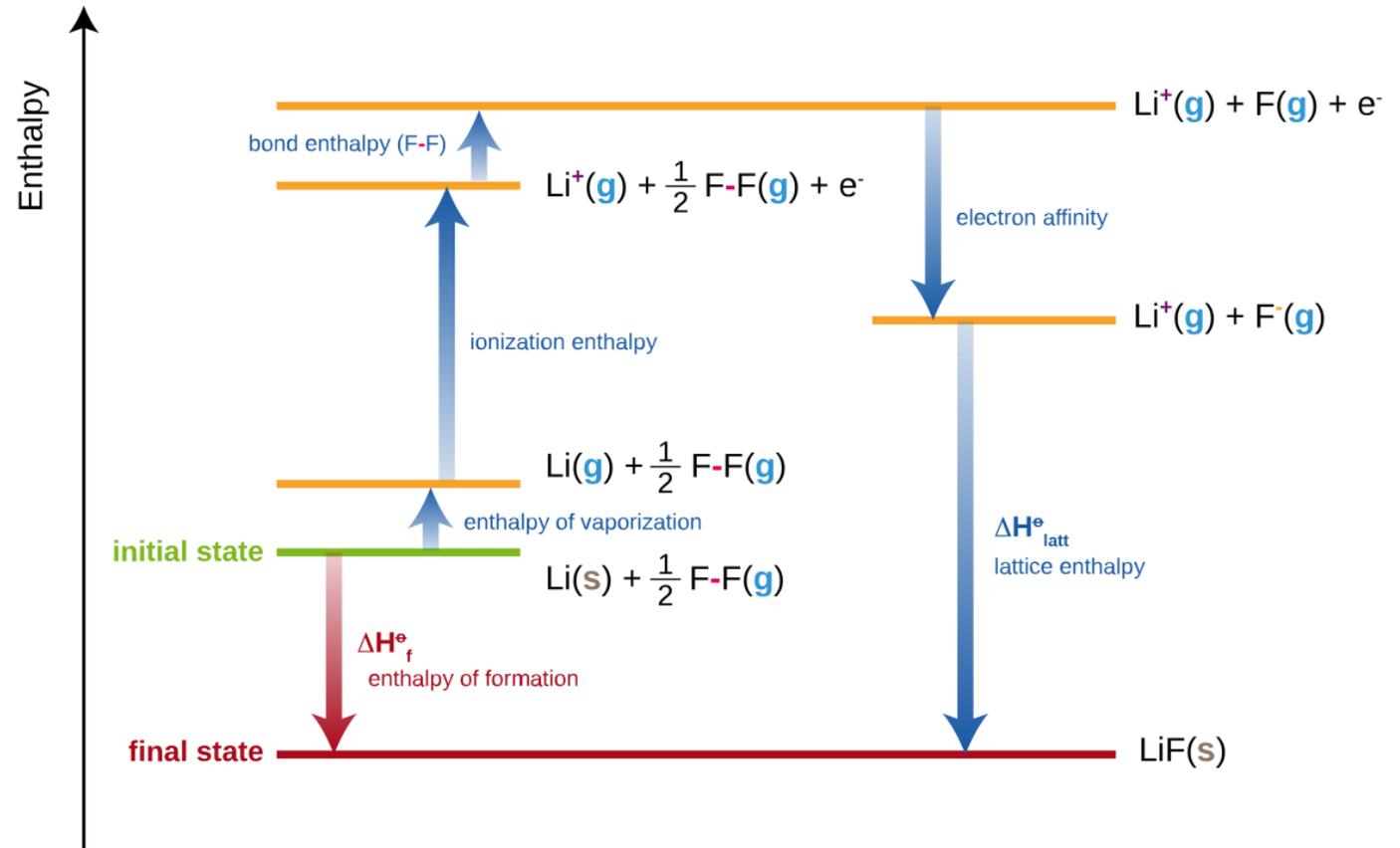
Thermochemistry

Background findings in history

- **Lavoisier and Laplace's law (1780):** The energy change in any transformation is equal and opposite to the energy change of the reverse process
- **Hess' law (1840):** The energy change in any transformation is the same whether the process happens in one or several steps.
 - State functions are not dependent on the path.

Born-Haber cycle

Born-Haber cycle is a method to analyze various reaction energies and bond energies in relation to Enthalpy of formation of an ionic compound



Standard enthalpy of a substance

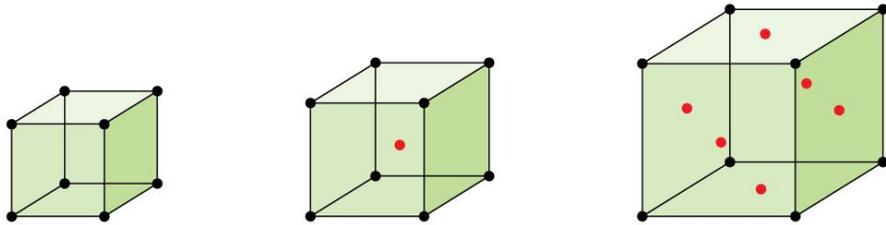
- Because numerical values are needed in the enthalpy and equilibrium calculations for reactions, the following definition has been chosen as zero for its 'scale':
- At 25 °C and 1 bar pressure the enthalpy of each element in its stable state (incl. the crystal structure) is zero or
- $H_{\text{SER}}(298.15 \text{ K}, 1 \text{ bar}) \equiv 0$.

Standard enthalpy of a substance

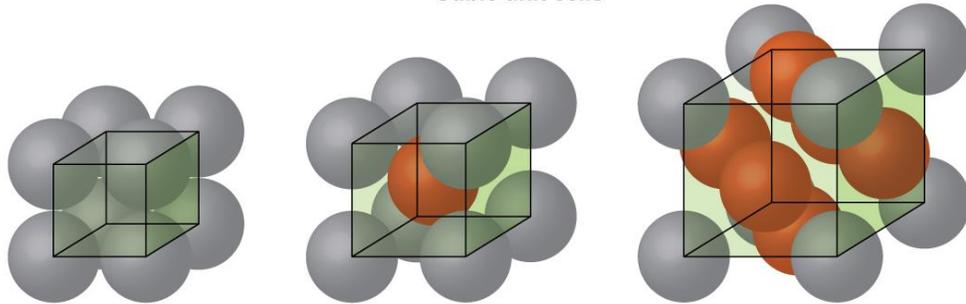
- For example, $H[\text{Cu}(\text{fcc}), 298.15 \text{ K}, 1 \text{ bar}] = 0$, but $H[\text{Cu}(\text{bcc}), 298.15 \text{ K}, 1 \text{ atm}] \neq 0$.
- Symbol of standard enthalpy is ${}^\circ H$, which is the value of enthalpy at 298.15 K and pressure of 1 bar.
- The enthalpies of all the other (unstable) forms of the elements and compounds can be determined experimentally with reference to this state ('reference state') and get them a numerical value.

Standard enthalpy of a substance

Lattice point locations



Cubic unit cells



Simple cubic

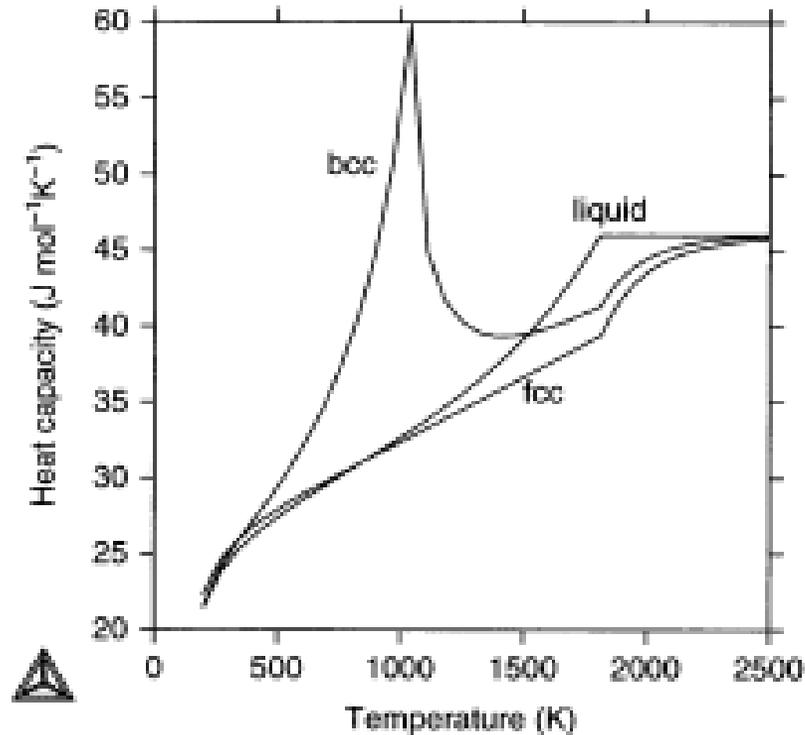
Body-centered cubic

Face-centered cubic

	$\Delta H_{f,298.15}$ J/mol	$S_{298.15}$ J/(mol K)	$\Delta G_{f,298.15}$ J/mol
Fe(bcc)	0	27.3	-8139.5
Fe(fcc)	7973	35.3	-2551.7
Cu(bcc)	4017	34.4	-6239.4
Cu(fcc)	0	33.15	-9883.7

Standard enthalpy of a substance

- The experimental technique for determining heat contents of materials is called 'calorimetry'.



c_p values of the various forms of iron.

About **entropy** of a substance

- In an *isobaric process* we get from previous equations for the change of entropy

$$dS = (d_q/T)_p = (dH/T)_p = c_p/T dT.$$

- In temperature variations of a closed system $T_1 \rightarrow T_2$ in constant pressure we therefore get for the change of entropy

$$\Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} c_p/T dT.$$

- At temperature T the entropy of a substance is thus

$$S(T) = S_0 + \int_0^T c_p/T dT$$

where S_0 is the entropy at the temperature of 0 K.

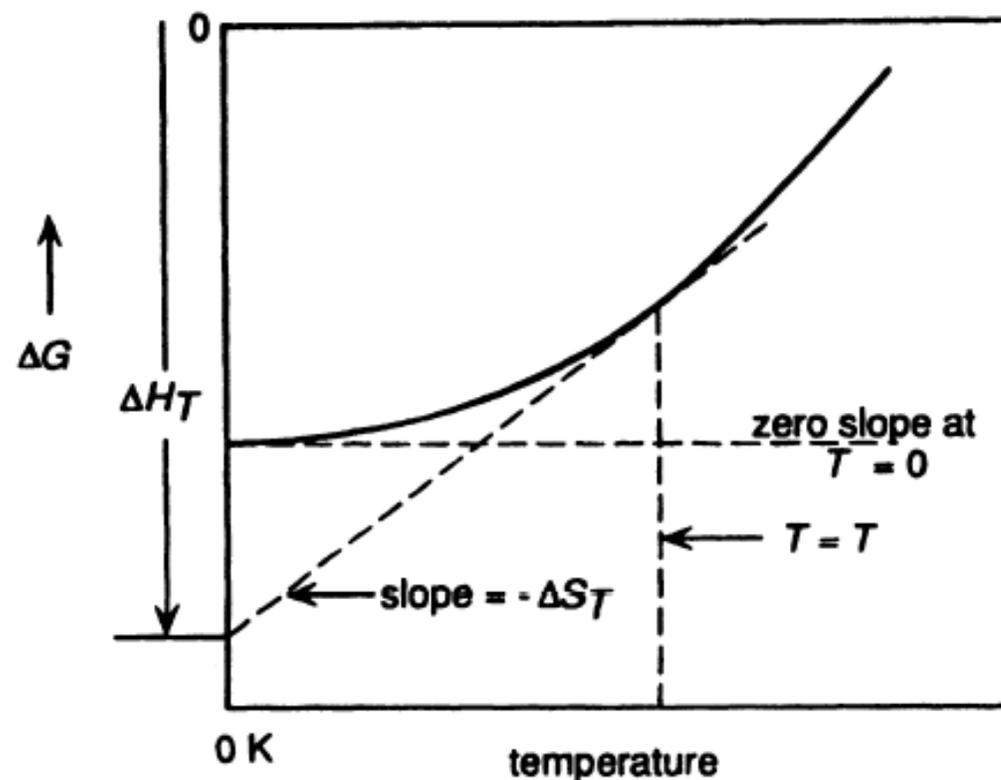
3rd law of thermodynamics

- Nernst postulated (1906) that the derivatives for chemical reactions of pure substances $(\partial\Delta G/\partial T)_p$ ja $(\partial\Delta H/\partial T)_p$ approach zero, when temperature approaches the absolute point of zero.

- In general, for a transformation of the system we get

$$\Delta G(T) = \Delta H(T) - T\Delta S(T)$$

the value of $\Delta S(T)$ must approach zero when approaching absolute zero point; in the same way behave the Δc_p value and all c_p functions.



...continues

- Max Planck *completed* the Nernst 'heat theorem' by defining the above behaviour to be valid for "all homogenous substances in complete internal equilibrium".
- This formulation today is called "**the 3rd law of thermodynamics**".

Standard entropy

- In addition to enthalpy of formation at 25 °C - or standard enthalpy - and c_p function, the third property of a substance controlling its stability is its **standard entropy** or (molar) entropy at 25°C (298.15 K).

- The equation derived earlier it has a general form of

$$S(T) = S_0 + \int_0^T c_p/T \, dT, \quad \text{when we select } T = 298.15 \text{ K.}$$

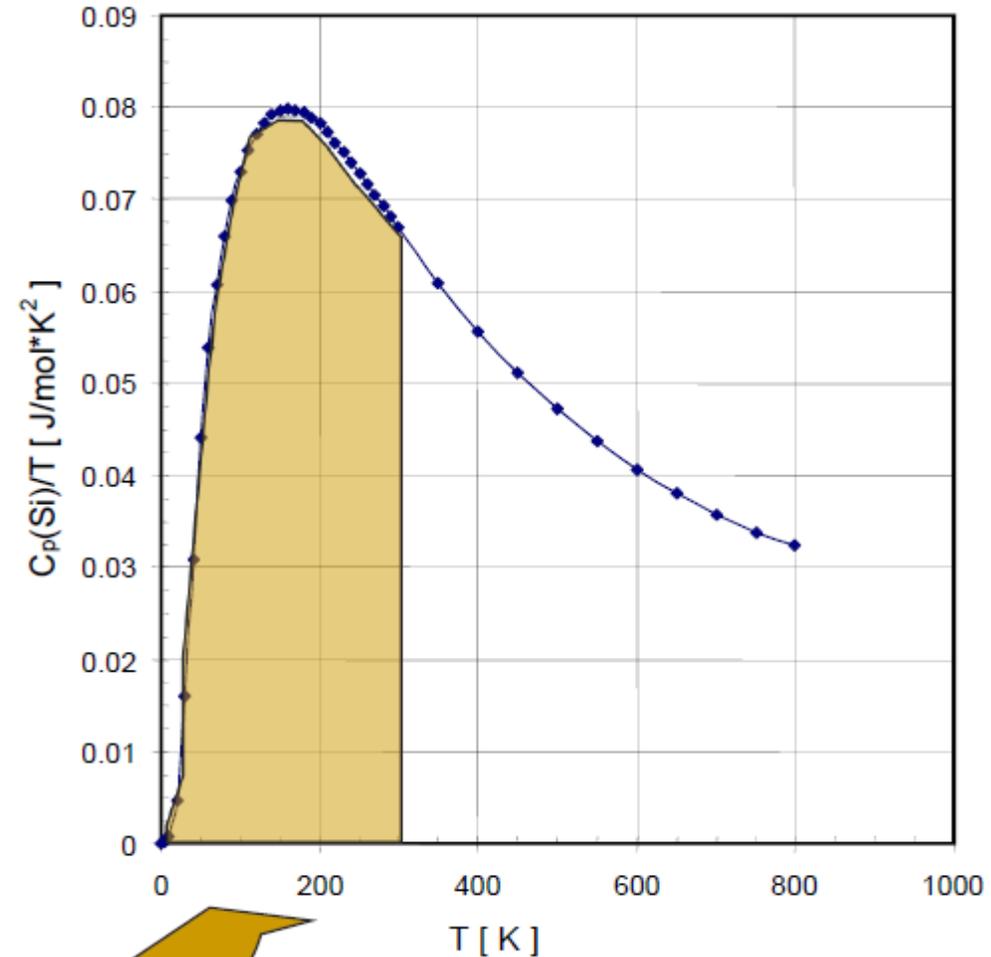
- 3rd law of thermodynamic gives $S_0 = 0$ and thus

$$S(298.15 \text{ K}) = \int_0^{298} c_p/T \, dT.$$

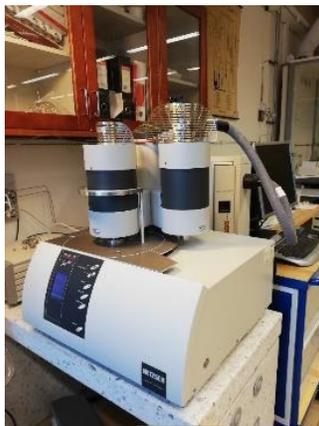
- The **standard entropy** is thus obtained from integral of its c_p/T 'behaviour' over the temperature range of 0-298.15 K.

.... continues

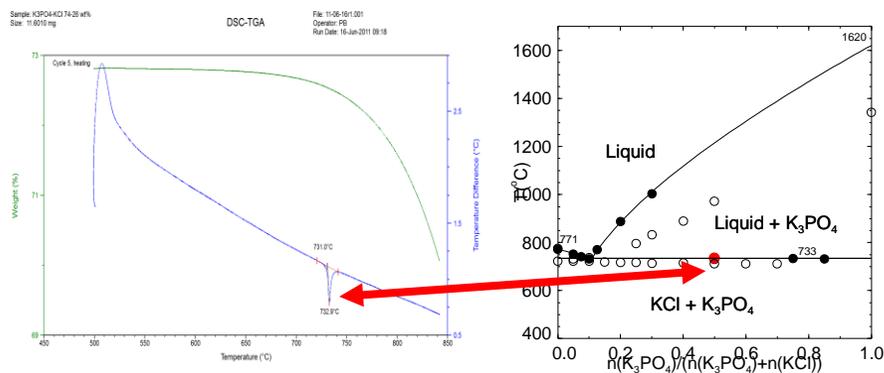
- Graph shows the experimental specific heat of silicon (Si) divided by temperature (c_p/T) as a function of T :
 - see that c_p/T approaches zero when T approaches 0 Kelvin.
 - c_p/T vs. T behaves well and is easy to integrate at 0-298.15 K.
 - $^\circ S(298)$ of a substance is thus the **area between abscissa axis and c_p/T plot** over the interval from 0 K to 298.15 K.



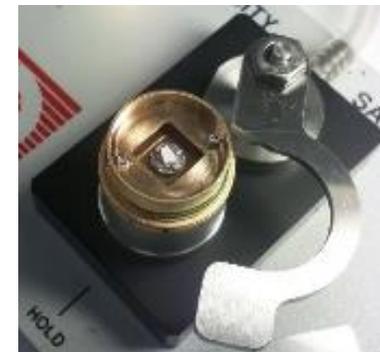
Differential scanning calorimetry



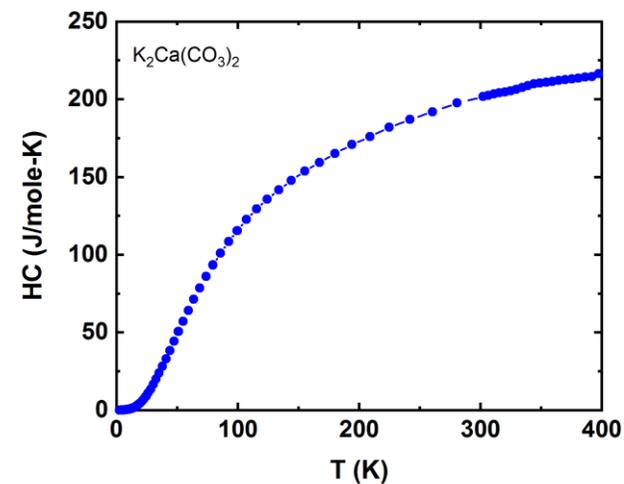
Phase transitions, high-T heat capacity and enthalpies of transition, evolved gases



Physical property measuring system PPMS



Low-T heat capacity and entropy of solid phases



Temperature dependence of S

- In thermodynamic handbooks entropy is given with standard entropy as reference; at $T > 298.15$ K we get

$$S(T) = {}^{\circ}S(298) + \int_{298}^T c_p/T \, dT.$$

- By inserting the Kelley equation of c_p to the equation we get at constant pressure

$$S(T) = {}^{\circ}S(298) + \int_{298}^T (a/T + b + c/T^3 + d \cdot T) \, dT.$$

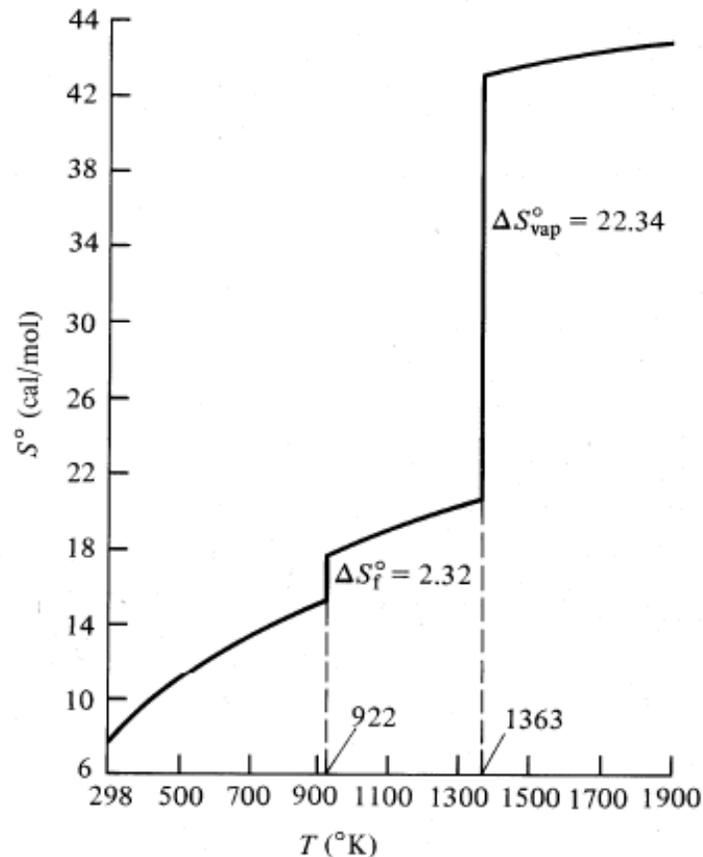
This is easy to integrate for getting the entropy at T.

- at temperature T we get for a homogenous 'volume':

$$S(T) = {}^{\circ}S(298) + a \ln(T/298) + b(T-298) - c/2(1/T^2 - 1/298^2) + d/2(T^2 - 298^2).$$

...continues

- The previous treatment gives entropy plot for each substance as a function of T which is discontinuous in a similar way and due to same reason as enthalpy.
- It has a discontinuity at phase transformation temperatures (e.g. isothermally) the magnitude of which is the *phase transformation entropy*.



- Such discontinuities, where
 - the value of entropy is discontinuous
 - its temperature derivative is not continuous either,all substances (except He in normal pressure) have at least two, melting point and boiling point (as a function of pressure).

The connection of phase transformation entropy with other measurable quantities

When two substances have same Gibbs energy the same pressure, they **are in equilibrium** with each other.

- Than in the point and at temperature T_{tr} of phase transformation we get for the phases α and β

$$G_{\alpha} = H_{\alpha} - T_{tr} \cdot S_{\alpha} \Leftrightarrow G_{\beta} = H_{\beta} - T_{tr} \cdot S_{\beta}$$

- Reorganising the terms, for the 'process' of phase transformation $\alpha \rightarrow \beta$:

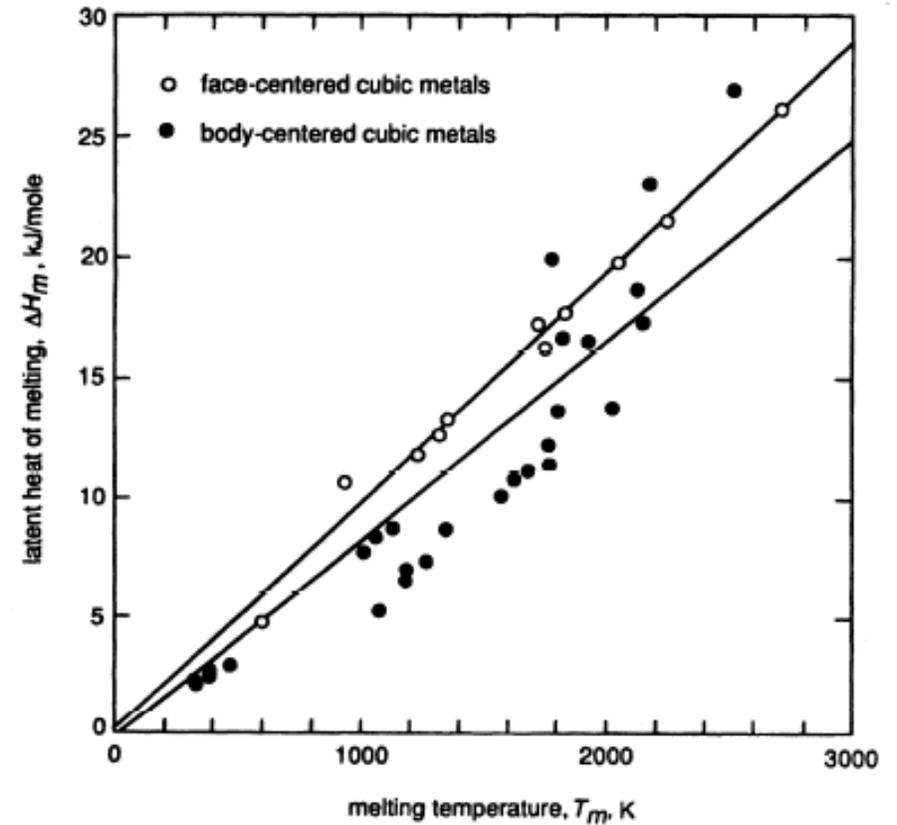
$$H_{\beta} - H_{\alpha} = \Delta_{tr}H(\alpha \rightarrow \beta) = T_{tr} \cdot [S_{\beta} - S_{\alpha}] = T_{tr} \cdot \Delta_{tr}S(\alpha \rightarrow \beta)$$

or

$$\Delta_{tr}S(\alpha \rightarrow \beta) = \Delta_{tr}H(\alpha \rightarrow \beta) / T_{tr}.$$

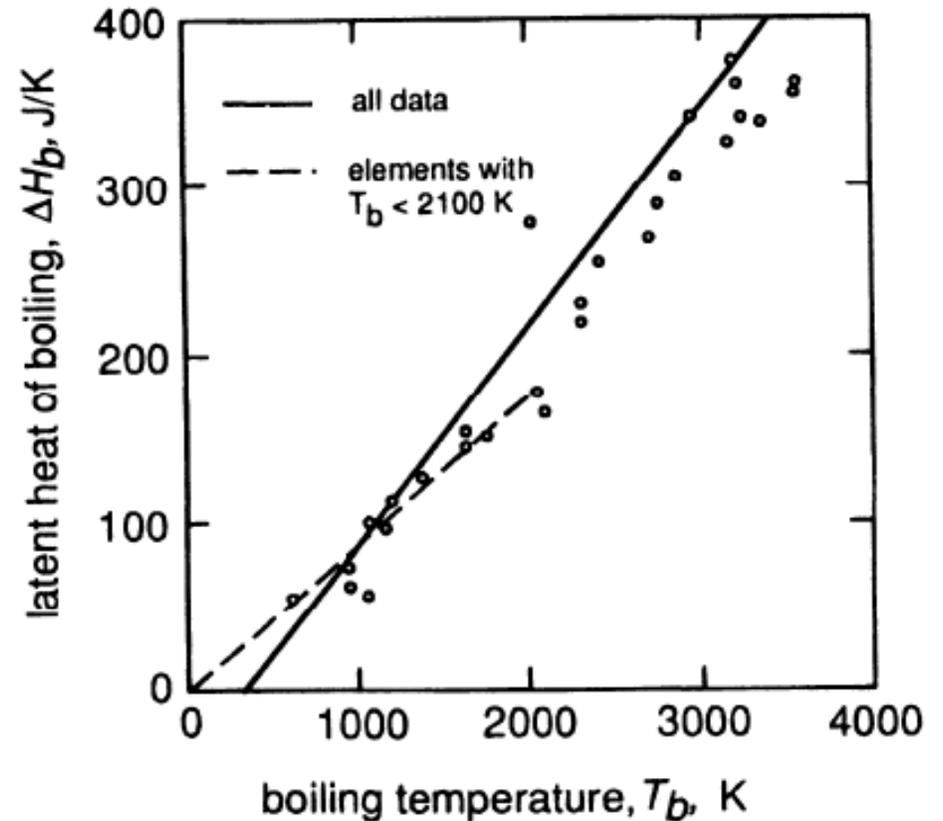
Richard's rule

- Richards postulated (1897) that the metals have an equally large entropy of melting.
- When we plot the enthalpy of melting as a function of melting point (K) we should get a straight line.
- Figure indicates that metals approximately follow this assumption, but the slope seems to be different in different crystal structures
 - the observation is useful if the properties of substances must be evaluated and there are no experimental data available.



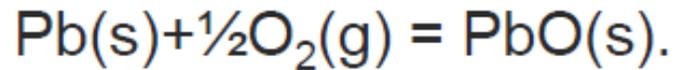
Trouton's rule

- In a similar way as Richards proposed for the melting points, Trouton suggested (1884) that the boiling entropy of substances at entropy (at boiling point) is constant and numerically about $22 \text{ cal}/(\text{K}\cdot\text{mol}) \approx 92 \text{ J}/(\text{K}\cdot\text{mol})$.
- The indicates that 13 molten *metals*, with the boiling point $<2100 \text{ K}$, have boiling entropy of $\approx 87 \text{ J}/(\text{K}\cdot\text{mol})$ and for 29 metals, with boiling point $<4000 \text{ K}$, it is $\approx 121 \text{ J}/(\text{K}\cdot\text{mol})$.



About entropy of reaction

- Let's look at a reaction of formation (i.e. cases with pure elements as raw materials and pure substance as product); an example is formation of lead (mon)oxide



- Its entropy of reaction is calculated from equation is

$$\Delta S_T = S_{T,\text{PbO}} - S_{T,\text{Pb}} - \frac{1}{2}S_{T,\text{O}_2(\text{g})}$$

- its order of magnitude is very close to the negative entropy of its gaseous raw material $-\frac{1}{2}S_{T,\text{O}_2(\text{g})}$. At the reference temperature 298.15 K we get

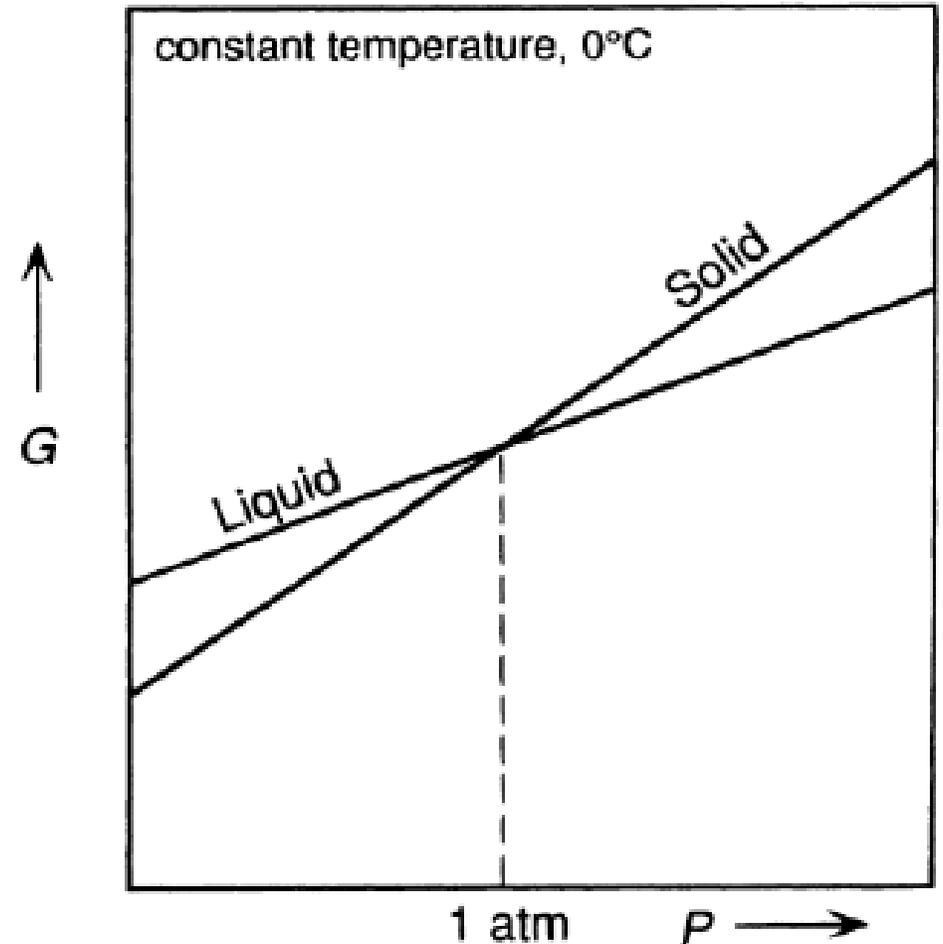
$$\Delta S(298) = S_{298,\text{PbO}} - S_{298,\text{Pb}} - \frac{1}{2}S_{298,\text{O}_2(\text{g})}, \quad 67.4 - 64.9 - \frac{1}{2} \cdot 205 = -100 \text{ J/K}.$$

- This is a **general 'rule'**: the change of entropy in the reaction is nearly as large as the contribution of the gas which *disappears* in the process.

Gibbs energy

Gibbs energy of pure substances is standard issue in thermodynamic handbooks, because it controls the equilibria.

- It is also a **state function**, (changes of) which can be measured experimentally.
- Temperature dependency of Gibbs energy function can be expressed using its c_p function, by simple arithmetic transformations using the relations described earlier.



Temperature dependence of Gibbs energy

- The general Gibbs energy definition gives, after inserting c_p function in equations of enthalpy and entropy:

$$G(T) = H(T) - S(T) \cdot T = {}^\circ H(298) + \int_{298.15}^T (a + b \cdot T + c/T^2 + d \cdot T^2) dT -$$

$$T \cdot [{}^\circ S(298) + \int_{298.15}^T (a + b \cdot T + c/T^2 + d \cdot T^2)/T dT] .$$

$$\int \frac{c_p}{T} dT$$

- After integration:

$$G(T) = a_0 + a_1 \cdot T - a \cdot T \cdot \ln T - b \cdot T^2/2 - c/(2 \cdot T) - d \cdot T^3/6$$

Temperature dependence of Gibbs energy

- The equation obtained resembles a lot the H and S functions, but the values of its a_0 and a_1 order terms' coefficients are not the standard enthalpy and entropy of the substance - they are combinations of a number of terms as

$$a_0 = {}^\circ\text{H}(298) - a \cdot 298.15 - b \cdot 298.15^2/2 + c/298.15 - d \cdot 298.15^3/3$$

and

$$a_1 = -{}^\circ\text{S}(298) + a \cdot (1 + \ln 298.15) + b \cdot 298.15 - c \cdot 298.15^{-2}/2 + d \cdot 298.15^2/2.$$

- These constants indicate that the mathematical form of Gibbs energy can be returned to the H and S functions, without any additional knowledge (than its cp function).
- This is the reason why many digital databases today store the values as G functions and not separate H and S functions (combined with the of terms of cpfunction).

Derivation of G function

Derive the G-function if C_p function is $a+bT+cT^{-2}+dT^2$, and ${}^\circ H(298)$ and ${}^\circ S(298)$ are known

$$G(T) = H(T) - T^*S(T)$$

$$H(T) = {}^\circ H(298) + \int_{298}^T C_p dT = {}^\circ H(298) + \int_{298}^T (a+bT+cT^{-2}+dT^2) dT$$

$$H(T) = {}^\circ H(298) + \int_{298}^T (aT + 1/2 bT^2 - cT^{-1} + 1/3 dT^3)$$

Derivation of G function

$$H(T) = {}^\circ H(298) + aT - a \cdot 298 + \frac{1}{2}bT^2 - \frac{1}{2}b \cdot 298^2 - \frac{c}{T} + \frac{c}{298} + \frac{1}{3}dT^3 - \frac{1}{3}d \cdot 298^3$$

$$H(T) = [{}^\circ H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + aT + \frac{1}{2}bT^2 - \frac{c}{T} + \frac{1}{3}dT^3$$

$${}^\circ H(298) = -20000$$

$${}^\circ S(298) = 300$$

$$a = 12$$

$$b = 0.05$$

$$c = 2500$$

$$d = 0.0005$$

Derivation of G function

Derive the G-function if C_p function is $a+bT+cT^{-2}+dT^2$, and $^\circ H(298)$ and $^\circ S(298)$ are known

$$G(T) = H(T) - T^*S(T)$$

$$S(T) = ^\circ S(298) + \int_{298}^T (C_p/T) dT = ^\circ S(298) + \int_{298}^T (a/T + b + cT^{-3} + dT) dT$$

$$S(T) = ^\circ S(298) + \int_{298}^T (a \ln T + bT - 1/2cT^{-2} + 1/2 dT^2)$$

Derivation of G function

$$S(T) = {}^\circ S(298) + a \ln T - a \ln(298) + bT - b \cdot 298 - \frac{1}{2}cT^2 + \frac{1}{2} \cdot \frac{c}{298^2} + \frac{1}{2}dT^2 - \frac{1}{2}d \cdot 298^2$$

$$S(T) = [{}^\circ S(298) - a \ln(298) - 298 \cdot b + \frac{c}{(2 \cdot 298^2)} - \frac{1}{2} \cdot 298^2 \cdot d] + a \ln T + bT - \frac{1}{2}cT^2 + \frac{1}{2}dT^2$$

$${}^\circ H(298) = -20000$$

$${}^\circ S(298) = 300$$

$$a = 12$$

$$b = 0.05$$

$$c = 2500$$

$$d = 0.0005$$

Derivation of G function

$$G(T) = H(T) - T \cdot S(T) = [\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + aT + \frac{1}{2}bT^2 - cT^{-1} + \frac{1}{3}dT^3 - T \cdot [\Delta S(298) - a \ln(298) - 298 \cdot b + \frac{c}{(2 \cdot 298^2)} - \frac{1}{2} \cdot 298^2 \cdot d] + a \ln T + bT - \frac{1}{2}cT^{-2} + \frac{1}{2}dT^2]$$

$$G(T) = [\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + aT + \frac{1}{2}bT^2 - cT^{-1} + \frac{1}{3}dT^3 - T \cdot \Delta S(298) + aT \ln 298 + bT \cdot 298 - \frac{cT}{(2 \cdot 298^2)} + \frac{1}{2}dT \cdot 298^2 - aT \ln T - bT^2 + \frac{1}{2}cT^{-1} - \frac{1}{2}dT^3$$

$$[\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + T[a \cdot \Delta S(298) + a \ln 298 + b \cdot 298 - \frac{c}{(2 \cdot 298^2)} + \frac{1}{2}d \cdot 298^2] + (\frac{1}{2}b - b)T^2 + (\frac{1}{3}d - \frac{1}{2}d)T^3 + (-c + \frac{1}{2}c) \cdot T^{-1} - aT \ln T$$

$$[\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + T[a \cdot \Delta S(298) + a \ln 298 + b \cdot 298 - \frac{c}{(2 \cdot 298^2)} + \frac{1}{2}d \cdot 298^2] - \frac{1}{2}bT^2 - \frac{1}{6}dT^3 - \frac{1}{2}c \cdot T^{-1} - aT \ln T$$

Derivation of G function

$$G(T) = [\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d] + T[a - \Delta S(298) + a \ln 298 + b \cdot 298 - \frac{c}{(2 \cdot 298^2)} + \frac{1}{2} d \cdot 298^2] - \frac{1}{2} b T^2 - \frac{1}{6} d T^3 - \frac{1}{2} c \cdot T^{-1} - a T \ln T$$

$$a_0 = [\Delta H(298) - 298a - \frac{1}{2} \cdot 298^2 \cdot b + \frac{c}{298} - \frac{1}{3} \cdot 298^3 \cdot d]$$

$$a_1 = [-\Delta S(298) + a(1 + \ln 298) + b \cdot 298 - \frac{c}{(2 \cdot 298^2)} + \frac{1}{2} d \cdot 298^2]$$

$$\Delta H(298) = -20000$$

$$\Delta S(298) = 300$$

$$a = 12$$

$$b = 0.05$$

$$c = 2500$$

$$d = 0.0005$$

Properties of pure substances

- **The substances can be divided into pure substances and mixtures:**
 - pure substance have a fixed (constant) composition
 - mixtures have variable compositions
- **The chemical behaviour of substances is controlled by their enthalpy and entropy:**
 - we need to know their P and T dependencies.
- **How they are given in the data compilations?**
 - the problem is that we do not know the value of internal energy in any system, only its differences; this means that also the value of enthalpy is unknown.
 - the (absolute) value of entropy can be measured by experimentation.

Thermodynamic tables

- Pure substance properties have been compiled in handbooks (JANAF, Barin etc.) and they are available also in various digital databases.
- Their data are fitted from experimental data by Kelley equation, usually over several temperature ranges.
- Computer-based (digital) databases may contain data about properties of metals in metastable conditions, i.e. for molten phase below melting point and in a similar way for solid phases outside their stability range.

Thermodynamic data in databases

- $G=f(T,P, n_i)= a+\sum bT^n+\sum cP^n\dots$
- $G(T)=H(T)-T\cdot S(T)$
- $H(T)=H(\text{ref})+\int_{T_{\text{ref}}}^T C_p dT$
- $S(T)=S(\text{ref})+\int_{T_{\text{ref}}}^T (C_p/T) dT$
- $C_p=a+bT+cT^{-2}+dT^n\dots$
- $G(T)=H(\text{ref})+\int_{T_{\text{ref}}}^T C_p dT - T\cdot [S(\text{ref})+\int_{T_{\text{ref}}}^T (C_p/T) dT]$

H(ref) and S(ref)

- Reference enthalpy of a compound is usually $\Delta_f H^\circ$ (298.15K)
- Enthalpy change for the formation of the compound from the elements in their stable form at 25 ° C
- $\Delta_f H^\circ$ (298.15K)_{CaO} = H(298.15K)_{CaO} - H(298.15K)_{Ca(s)} - ½ H(298.15K)_{O2(g)}

$$H(T) = \Delta_f H^\circ (298.15K) + \int_{298}^T C_p dT$$

- Reference entropy is usually absolute entropy defined from the third law of thermodynamics S° (298.15K)

$$S(T) = \int_0^T (C_p/T) dT \quad \text{or} \quad S(T) = S^\circ (298.15K) + \int_{298}^T (C_p/T) dT$$

$$G(T) = \Delta_f H^\circ (298.15K) + \int_{298}^T C_p dT - T \cdot [S^\circ (298.15K) + \int_{298}^T (C_p/T) dT]$$

Nickel sulfide (NiS)

Nickel Sulfide (NiS)

CRYSTAL(RHOMBOHEDRAL-HEXAGONAL)

$M_r = 90.75$ Nickel Sulfide (NiS)

$\text{Ni}_1\text{S}_1(\text{cr})$

1704

$S^\circ(298.15 \text{ K}) = 52.992 \pm 0.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{trs}} = 652 \pm 3 \text{ K}$
 $T_{\text{fus}} = 1249 \pm 3 \text{ K}$

$\Delta_f H^\circ(0 \text{ K}) = -87.13 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = -87.86 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{tr}} H^\circ = 6.443 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{fus}} H^\circ = 30.125 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

Rosenqvist¹ studied the sulfur vapor pressure above solid nickel sulfides using the $\text{N}_2/\text{H}_2\text{S}$ equilibrium. Combining his data for several equilibria we calculate 2nd and 3rd law values of $\Delta_f H^\circ(298.15 \text{ K})$ for NiS(cr) to be $20.5 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$ and $-22.6 \pm 3.6 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. The stoichiometry of NiS varies from at least NiS_{0.98} to NiS_{1.06} and Ariya *et al.*² investigated $\Delta_f H^\circ(298.15 \text{ K})$ in the composition range by calorimetric methods. These authors found $\Delta_f H^\circ(298.15 \text{ K}) = -20.3 \pm 0.6 \text{ kcal}\cdot\text{mol}^{-1}$ for stoichiometric NiS with an ill-defined trend toward more exothermic values at higher sulfur content. DeRanter and Breckpot³ obtained a value of $20.08 \text{ kcal}\cdot\text{mol}^{-1}$ for amorphous Ni_{0.98}S from an enthalpometric titration. We calculate $\Delta_f H^\circ(298.15 \text{ K}) = -21.3 \text{ kcal}\cdot\text{mol}^{-1}$ for the same material based on a 3rd law analysis of DeRanter and Breckpot's emf data.³

In view of the rather large uncertainties and variations due to stoichiometry we choose to adopt the average of the five values above, $\Delta_f H^\circ(298.15 \text{ K}) = -21.0 \pm 1.5 \text{ kcal}\cdot\text{mol}^{-1}$. This value is somewhat less negative than values of -22.1 and $-22.5 \text{ kcal}\cdot\text{mol}^{-1}$ adopted by Mah and Pankrantz⁴ and Mills,⁵ respectively.

Heat Capacity and Entropy

The low temperature heat capacity data (52–296 K) are taken from Weller and Kelley.⁶ High temperature enthalpies of NiS_{1.03} were measured by Conard *et al.*⁷ via drop calorimetry. We have joined these values smoothly with the low temperature C_p° measurements of Weller and Kelley⁶ to derive the C_p° values from 298–652 K. Values of C_p° above the transition are also taken from our analysis of Conard's *et al.*⁷ enthalpy data, disregarding the points above 1000 K to avoid problems due to incongruent melting. Values above 1000 K are extrapolated.

Phase Data

Both the low (β) and high (α) temperature polymorphs of NiS dissolve excess sulfur to form solid solutions. The β phase shows a limited range of homogeneity but the α phase shows a broad limit extending to approximately NiS_{1.10}.⁸ The α phase is normally designated $\alpha\text{-Ni}_{1-x}\text{S}$ to emphasize this feature. However, the sulfur-poor limit of this phase has the stoichiometric composition to at least 873 K; at 1070 K the deviation from stoichiometry is less than 0.05 weight % nickel.⁸ Above 1079 K the deviation of the sulfur-poor limit from stoichiometry increases more rapidly and a material of stoichiometry NiS will exist as an equilibrium mixture of liquid Ni_{1-x}S₂ and solid $\alpha\text{-Ni}_{1-x}\text{S}.⁸ Thus, NiS melts incongruently.$

Transition Data

We adopt $652 \pm 3 \text{ K}$ as the transition temperature of stoichiometric NiS from rhombohedral (β) to hexagonal (α) form base on the phase diagram of Kullerud and Yund.⁸ The temperature of this transition is very dependent on the exact stoichiometry of the material.⁸ The transition enthalpy has been measured via a DTA technique by Conard *et al.*⁷ and we adopt their value of $1.54 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$. This is considerably higher than an older value of $0.63 \text{ kcal}\cdot\text{mol}^{-1}$ measured by Biltz *et al.*^{9,5} but should be much more accurate due to the calibration technique used. Mah and Pankrantz⁴ estimated $0.7 \text{ kcal}\cdot\text{mol}^{-1}$. This transition enthalpy cannot be measured by drop calorimetry since the α form does not revert to the β form on cooling.

Fusion Data

As stated above, stoichiometric NiS will begin to form a liquid at 1079 K. The conversion to stoichiometric liquid NiS is complete at 1249 K.⁸ We adopt the latter as the melting point of NiS with an uncertainty estimated to be $\pm 3 \text{ K}$. The adopted heat of melting, $\Delta_{\text{fus}} H^\circ = 7.20 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$, is from our analysis of the high temperature enthalpy data of Conard *et al.*⁷ This value compares favorably with estimated values of 7.4 and $7.0 \text{ kcal}\cdot\text{mol}^{-1}$ due to Nagamori and Ingraham¹⁰ and Mah and Pankrantz.⁴

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- ⁹W. Biltz, F. Weibke, P. Ehrlich, and K. Meisel, Z. Anorg. Chem. **228**, 275 (1936).
- ¹⁰M. Nagamori and T. R. Ingraham, Met. Trans. **1**, 1821 (1970).

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$					
T/K	C_p°	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		$\text{kJ}\cdot\text{mol}^{-1}$			
		S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_r$
0	0	0	INFINITE	-8.465	-87.131	-87.131	INFINITE
100	23.187	12.857	89.876	-7.702	-87.566	-86.854	45.368
200	40.626	35.370	57.135	-4.353	-87.748	-86.055	22.475
298.15	47.112	52.992	52.992	0	-87.864	-85.200	14.927
300	47.196	53.284	52.993	0.087	-87.867	-85.184	14.832
400	50.501	67.332	54.886	4.978	-90.301	-84.172	10.992
500	53.053	78.880	58.563	10.158	-92.016	-82.453	8.614
600	55.312	88.757	62.792	15.579	-93.458	-80.402	7.000
652.000	56.372	93.399	65.050	18.483		BETA <- -> ALPHA	
652.000	53.152	103.281	65.050	24.927		TRANSITION	
700	54.518	107.105	67.804	27.511	-88.196	-78.598	5.865
800	57.363	114.570	73.189	33.105	-88.900	-77.175	5.039
900	60.208	121.491	78.176	38.983	-142.408	-74.603	4.330
1000	63.053	127.982	82.835	45.146	-141.290	-67.127	3.506
1100	65.898	134.125	87.221	51.594	-139.971	-59.773	2.838
1200	68.743	139.980	91.375	58.326	-138.456	-52.547	2.287
1249.000	70.137	142.759	93.337	61.728		ALPHA <- -> LIQUID	
1300	71.588	145.595	95.332	65.342	-136.751	-45.456	1.826
1400	74.433	151.005	99.116	72.644	-134.864	-38.503	1.457
1500	77.278	156.237	102.751	80.229	-132.797	-31.691	1.104
1600	80.124	161.315	106.253	88.099	-130.554	-25.023	0.817
1700	82.969	166.258	109.638	96.254	-128.142	-18.500	0.568

Adopted values + uncertainties are given

Reasons for data preferences are given

MALCOLM W. CHASE

PREVIOUS:

CURRENT: December 1976

Nickel Sulfide (NiS)

$\text{Ni}_1\text{S}_1(\text{cr})$

Energy: Joules Pressure: bar SiO2

File Edit Units View Tools ViewData Help

Formula SiO2

ANODBASE
BINSBASE
CARBBASE
CHEMBASE
ELEMBASE
FACT53BASE
SiO2
S1
S2
S3
S4
S5
S6
S7
S8
L1
FACTBASE
FThallBASE
FThelgBASE
FTmiscBASE
FToxidBASE
FTpulpBASE

S1 properties
 Heat of form. + Entropy Heat + Temperature of transf.

Form. of S1
 ΔH_{298} (Joules) S_{298} (J/(mol K))
 [-910699.94184] [41.4600015888]

Phase Name Reference no. Density g/cc
 Quartz(l) 132 149 2.649

Extended properties (optional)
 Birch-Murnaghan

Therm. expans. (/K)		Compressibility (/bar)		Bulk mod. deriv.	
2.7513E-5		2.556E-6		6.4	
2.9868E-8	T	1.1557E-11	T	0.01	T ln(T)
5.5722E-6	/T	1.0128E-16	T^2		
0.091181	/T^2	8.89179E-19	T^3		

Magnetic Moment (D) Temperature P factor
 Curie K 0.28
 Neel 0.40

FactSage 6.2 C:\FactSage\FACTDATA\FS53base.cdb (v5.0) 4557 compounds read-only

Energy: Joules Pressure: bar SiO2

File Edit Units View Tools ViewData Help

Formula SiO2

ANODBASE
BINSBASE
CARBBASE
CHEMBASE
ELEMBASE
FACT53BASE
SiO2
S1
Cp 373
Cp 848
Cp 850
S2
S3
S4
S5
S6
S7
S8
L1
FACTBASE
FThallBASE
FThelpBASE

Cp expression for S1
 ΔH_{298} : -910699.94184 J/mol
 S_{298} : 41.4600015887999 J/(mol K)
 from 298.150 K to 373.000 K

Cp
 H
 S
 G Edit

Cp(T) =	80.0119918	T ^{0.00}
		T ^{1.00}
	-3546683.99888	T ^{-2.00}
		T ^{2.00}
	-240.275998928	T ^{-0.50}
	491568369.44	T ^{-3.00}
		T
		T

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Energy: Joules Pressure: bar SiO2

File Edit Units View Tools ViewData Help

Formula SiO2

ANODBASE
 BINSBASE
 CARBBASE
 CHEMBASE
 ELEMBASE
 FACT53BASE
 SiO2
 S1
 Cp 373
 Cp 848
 Cp 850
 S2
 S3
 S4
 S5
 S6
 S7
 S8
 L1
 FACTBASE
 FThallBASE
 FThelpBASE

G expression for S1

ΔH_{298} : -910699.94184 J/mol
 S_{298} : 41.4600015887999 J/(mol K)
 from 298.150 K to 373.000 K

Cp
 H
 S
 G Edit

G(T) =

-935388.521317283	T^0.00
536.02534211745	T^1.00
-80.0119918	T ln T
	T^2.00
	T^3.00
1773341.99944	T^-1.00
-961.103995712	T^0.50
-81928061.5733333	T^-2.00
	T^
	T^

Note: T^99 => ln T

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Energy: Joules Pressure: bar SiO2

File Edit Units View Tools ViewData Help

Formula SiO2

ANODBASE
BINSBASE
CARBBASE
CHEMBASE
ELEMBASE
FACT53BASE
SiO2
S1
S2
S3
S4
S5
S6
S7
S8
L1
FACTBASE
FThallBASE
FThelgBASE
FTmiscBASE
FToxidBASE
FTnulpBASE

S1 properties
 Heat of form. + Entropy Heat + Temperature of transf.

Form. of S1
 ΔH_{298} (Joules) S298 (J/(mol K))
 -910699.94184 41.4600015888

Phase Name Reference no. Density g/cc
 Quartz(l) 132 149 2.649

Extended properties (optional)

Birch-Murnaghan

Therm. expans. (/K)		Compressibility (/bar)		Bulk mod. deriv.	
2.7513E-5		2.556E-6		6.4	
2.9868E-8	T	1.1557E-11	T	0.01	T ln(T)
5.5722E-6	/T	1.0128E-16	T^2		
0.091181	/T^2	8.89179E-19	T^3		

Magnetic Moment (D) Temperature P factor
 Curie K 0.28
 Neel 0.40

FactSage 6.2 C:\FactSage\FACTDATA\FS53base.cdb (v5.0) 4557 compounds read-only

Extended properties