Entropy of Reaction

By

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Entropy

- Consider a reversible process in which the system absorbs in a reversible manner an infinitesimal quantity of heat δq at temperature T. The term δq/T is called the entropy change.

$$ds = \frac{\delta q_{rev}}{T}$$

- For a reversible process, the sum of the entropy change of the system and of the surroundings is always zero, i.e.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

- For an irreversible, i.e. spontaneous, process the sum of the entropy change of the system and its surroundings is a positive quantity, i.e.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Calculating entropy changes

1) Entropy changes during change of state:

These changes occur at constant temperature and are reversible

$$\Delta S^{\ominus} = \begin{cases} L_{\mathrm{f}}/T_{\mathrm{m}} & \text{for fusion} \\ L_{\mathrm{e}}/T_{\mathrm{b}} & \text{for vaporisation} \end{cases}$$

where L_f and L_e are molar latent heats of fusion and evaporation respectively, and T_m and T_b are the melting and boiling point temperatures respectively.

2) Entropy changes during change of temperature:

$$\Delta S^{\ominus} = S_2^{\ominus} - S_1^{\ominus} = \int_{T_1}^{T_2} \frac{\mathrm{d}q_{\mathrm{rev}}}{T} \qquad (1)$$

but referring to Kirchoff's equation and assuming that heat absorbed, q_{rev} can be substituted by ΔH (since at constant pressure, $q_{rev} = \Delta H_{rev}$) then

$$\frac{dq_{rev}}{dT} = \Delta C_p$$

$$dq_{rev} = \Delta C_p dT$$

so that equation (1) becomes

$$\Delta S^{\ominus} = S_2^{\ominus} - S_1^{\ominus} = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT \qquad (2)$$

Integration of equation (2) yields,

$$\Delta S^{\ominus} = S_2^{\ominus} - S_1^{\ominus} = C_p \ln(T_2/T_1) \qquad (3)$$

The absolute entropy can also be found by considering entropies at an arbitrary temperature T and at absolute zero. In this case

$$\Delta S^{\ominus} = S_T^{\ominus} - S_0^{\ominus}$$

but $S_0^{\ominus} = 0$ by the third law of thermodynamics and so

$$\Delta S^{\ominus} = S_T^{\ominus}$$

Hence for high temperature conditions it is convenient to use equation (3) in the form:

$$\Delta S_T^{\ominus} = S_{298}^{\ominus} + C_p \ln(T/298)$$

3) Entropy changes during chemical reactions:

a) At 298 K

$$\Delta S_{298}^{\ominus} = S^{\ominus}_{\text{prods, 298}} - S^{\ominus}_{\text{reacts, 298}}$$

b) At any temperature *T* *with* phase transformation

$$S^{o}_{T_2} = S^{o}_{T_1} + \int_{T_1}^{T'} \frac{C_p'}{T}\, dT + \frac{H_t}{T'} + \int_{T'}^{T_2} \frac{C_p''}{T}\, dT$$

where Cp’ and Cp” are the heat capacities of the substance before and after the transformation, respectively, and ΔH_t is the enthalpy change of the transformation.

If there is more than one transformation, then entropy changes for all the transformations must be included.

A similar equation can be derived for chemical reactions involving phase transformations either in reactants, products, or both.

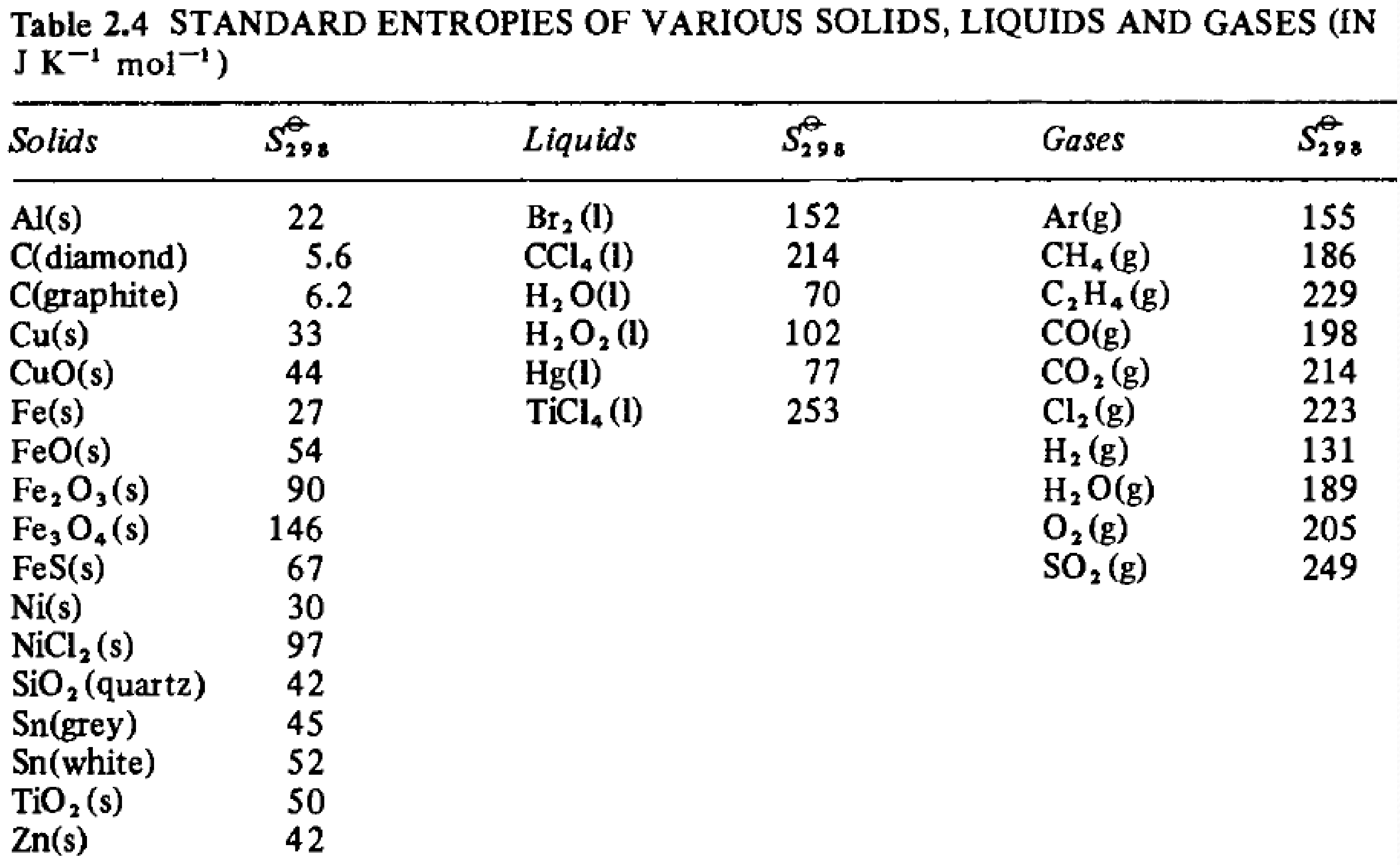
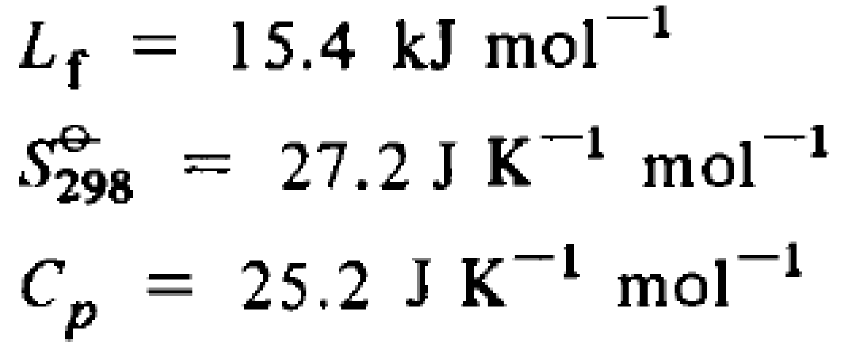


Table 2.4 STANDARD ENTROPIES OF VARIOUS SOLIDS, LIQUIDS AND GASES (IN J K^{-1} mol^{-1})

Solids	$S^\ominus_{298}$	*Liquids*	$S^\ominus_{298}$	*Gases*	$S^\ominus_{298}$
Al(s)	22	Br_2(l)	152	Ar(g)	155
C(diamond)	5.6	CCl_4(l)	214	CH_4(g)	186
C(graphite)	6.2	H_2O(l)	70	C_2H_4(g)	229
Cu(s)	33	H_2O_2(l)	102	CO(g)	198
CuO(s)	44	Hg(l)	77	CO_2(g)	214
Fe(s)	27	$TiCl_4$(l)	253	Cl_2(g)	223
FeO(s)	54			H_2(g)	131
Fe_2O_3(s)	90			H_2O(g)	189
Fe_3O_4(s)	146			O_2(g)	205
FeS(s)	67			SO_2(g)	249
Ni(s)	30				
$NiCl_2$(s)	97				
SiO_2(quartz)	42				
Sn(grey)	45				
Sn(white)	52				
TiO_2(s)	50				
Zn(s)	42				

Example (1)

Calculate the entropy of liquid iron at its melting point, 1808 K, given that, for iron



$$L_f = 15.4\ \text{kJ mol}^{-1}$$

$$S^\ominus_{298} = 27.2\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$C_p = 25.2\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Homework

In each case values of for substances can be obtained by reference to *Table 2.4.*

(1) If 30.8 kJ of heat are supplied to a mixture of benzene and its vapour at 353 K, one mole of benzene is vaporised. Calculate the change in entropy for this process.

(3) Calculate the standard entropy of copper at 1800 K, given that, for copper, $T_m = 1356$ K, $C_p = 24.5$ J K^{-1} mol^{-1} (assumed constant in the region 298–1800 K), $L_f = 13.0$ kJ mol^{-1} and $\Delta S^{\ominus}_{298}$ [Cu(s)] = 33.3 J K^{-1} mol^{-1}

(4) For the reaction

$$TiO_2(s) + 2Cl_2(g) + C(s) \xrightarrow{298\ K} TiCl_4(l) + CO_2(g)$$

Calculate: (a) $\Delta S^{\ominus}_{298}$ and (b) $\Delta S^{\ominus}_{798}$, the temperature at which the commercial reaction is carried out. Between 298 K and 798 K only $TiCl_4$ goes through a transformation and the molar heat capacities (assumed constant over the temperature range) required are as follows:

	$TiO_2(s)$	$Cl_2(g)$	$C(s)$	$TiCl_4(g)$	$CO_2(g)$
C_p (J K^{-1} mol^{-1})	55	40	8.6	157	37

$T_b = 413$ K $\quad L_e = 138.6$ kJ mol^{-1}

Criterion of Spontaneity Based on Entropy

For a chemical reaction proceeding from the initial state A to the final state B, the total entropy change, i.e. that of the system and its surroundings, can be written as

$$\Delta S_{total} = S_{B,total} - S_{A,total}.$$

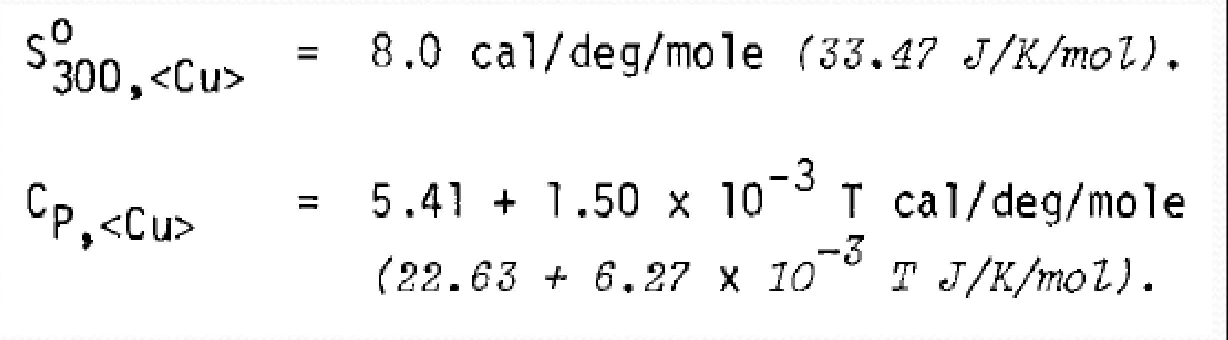
Under the restricted conditions of constant U and V, or constant H and P, the following criteria can be utilized in assessing the probability of spontaneous change in the system:

1) If $\Delta S_{total} = 0$, the system is at equilibrium and no spontaneous change will occur.

2) If $\Delta S_{total} > 0$ the reaction will tend to occur spontaneously from state A to state B.

3) If $\Delta S_{total} < 0$, the reaction will tend to occur spontaneously in the reverse direction, i.e. from state B to state A.

Example (2) Calculate the standard entropy of solid copper at 1073°C from the following data:



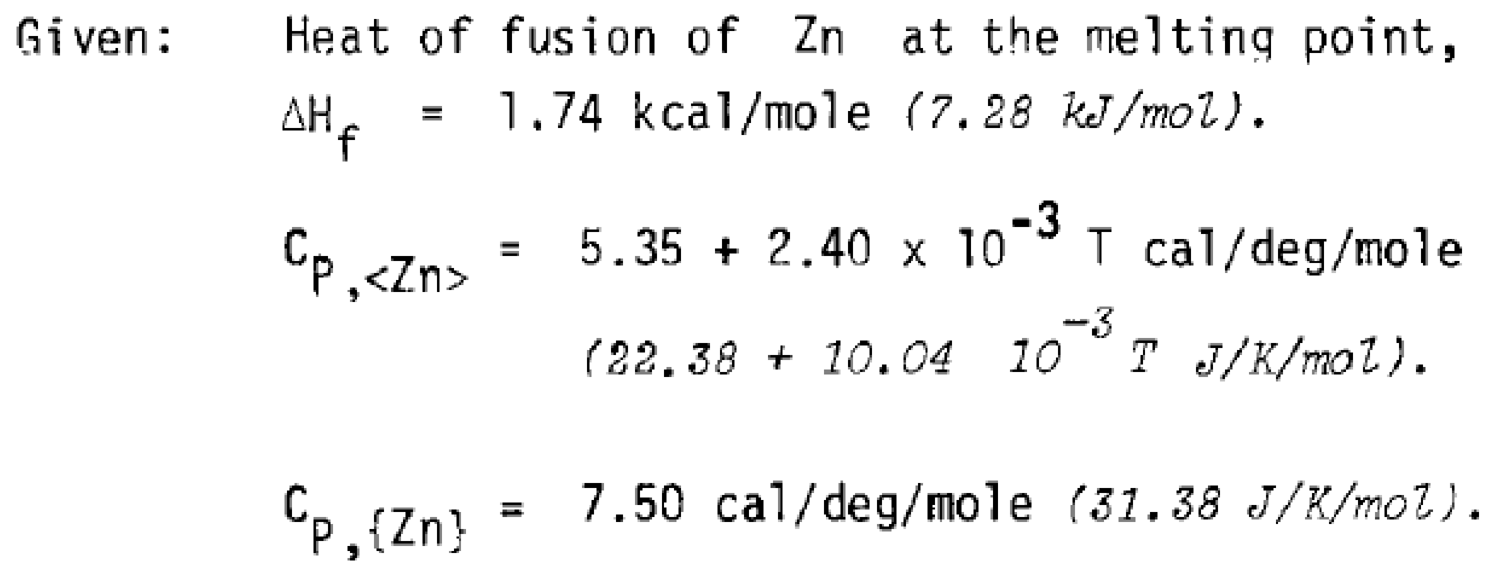
$S^{o}_{300,<Cu>}$ = 8.0 cal/deg/mole *(33.47 J/K/mol).*

$C_{P,<Cu>}$ = $5.41 + 1.50 \times 10^{-3}$ T cal/deg/mole

($22.63 + 6.27 \times 10^{-3}$ T J/K/mol).

Example (3)

Zinc melts at 420°Cand its standard entropy at 25°C is 9.95 cal/deg/mole. Calculate the standard entropy of zinc at 750°C



Given: Heat of fusion of Zn at the melting point,

ΔH_f = 1.74 kcal/mole *(7.28 kJ/mol).*

$C_{P,<Zn>}$ = $5.35 + 2.40 \times 10^{-3}$ T cal/deg/mole

($22.38 + 10.04 \; 10^{-3}$ T J/K/mol).

$C_{P,\{Zn\}}$ = 7.50 cal/deg/mole *(31.38 J/K/mol).*

Example (4)

The phase transformation in pure iron may be represented as follows:

$$\langle\alpha\text{-Fe}\rangle \xrightarrow{1033K} \langle\beta\text{-Fe}\rangle \xrightarrow{1183K} \langle\gamma\text{-Fe}\rangle \xrightarrow{1673K} \langle\delta\text{-Fe}\rangle \xrightarrow{1812K} \{\text{Fe}\}.$$

Calculate the standard entropy of pure iron at 1627°C (*1900 K*) if its standard entropy at 25°C (*298 K*) is 6.50 cal/deg/mole (*27.20 J/K/mol*).

Given: $C_{P,\langle\alpha\text{-Fe}\rangle} = 4.18 + 5.92 \times 10^{-3}\,T$ cal/deg/mole

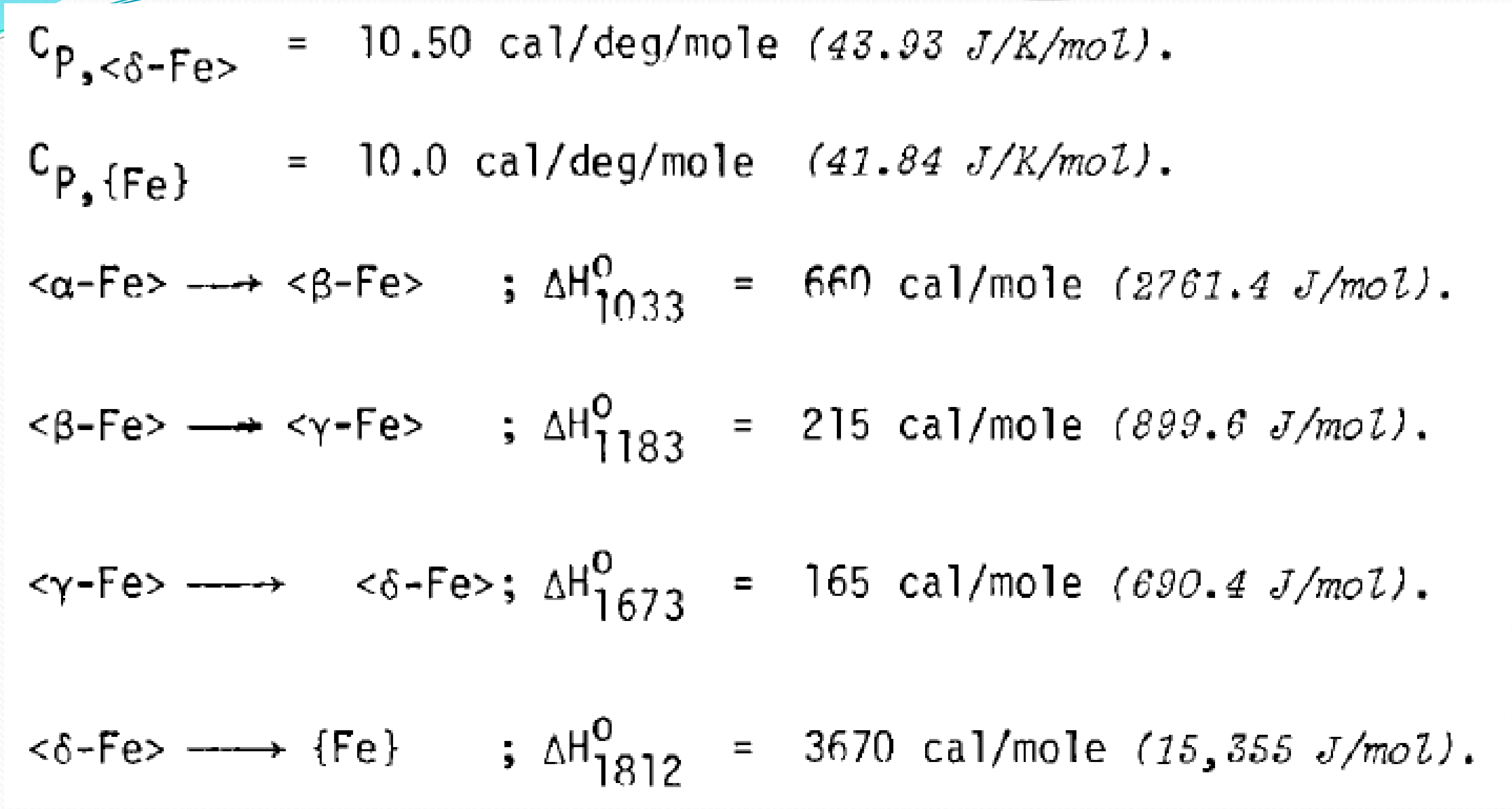
($17.49 + 24.77 \times 10^{-3}\,T$ J/K/mol).

$C_{P,\langle\beta\text{-Fe}\rangle} = 9.0$ cal/deg/mole

(37.66 J/K/mol).

$C_{P,\langle\gamma\text{-Fe}\rangle} = 1.84 + 4.66 \times 10^{-3}\,T$ cal/deg/mole

($7.70 + 19.50 \times 10^{-3}\,T$ J/K/mol).



$C_{P,<\delta\text{-Fe}>} = 10.50$ cal/deg/mole *(43.93 J/K/mol)*.

$C_{P,\{\text{Fe}\}} = 10.0$ cal/deg/mole *(41.84 J/K/mol)*.

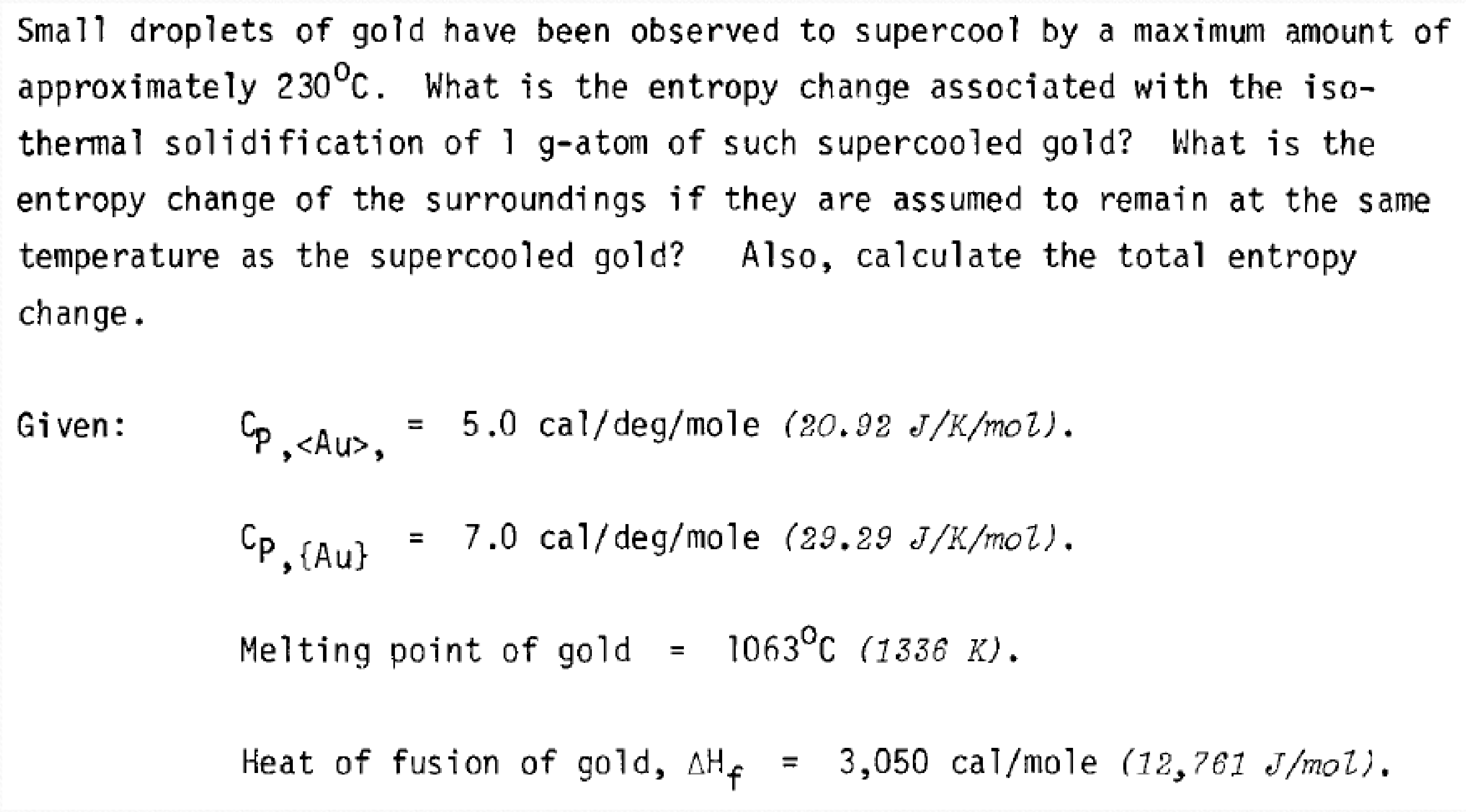
$<\alpha\text{-Fe}> \longrightarrow <\beta\text{-Fe}>$; $\Delta H^{o}_{1033} = 660$ cal/mole *(2761.4 J/mol)*.

$<\beta\text{-Fe}> \longrightarrow <\gamma\text{-Fe}>$; $\Delta H^{o}_{1183} = 215$ cal/mole *(899.6 J/mol)*.

$<\gamma\text{-Fe}> \longrightarrow <\delta\text{-Fe}>$; $\Delta H^{o}_{1673} = 165$ cal/mole *(690.4 J/mol)*.

$<\delta\text{-Fe}> \longrightarrow \{\text{Fe}\}$; $\Delta H^{o}_{1812} = 3670$ cal/mole *(15,355 J/mol)*.

Example (5)



Small droplets of gold have been observed to supercool by a maximum amount of approximately 230°C. What is the entropy change associated with the isothermal solidification of 1 g-atom of such supercooled gold? What is the entropy change of the surroundings if they are assumed to remain at the same temperature as the supercooled gold? Also, calculate the total entropy change.

Given: $C_{P,\langle Au\rangle,}$ = 5.0 cal/deg/mole *(20.92 J/K/mol)*.

$C_{P,\{Au\}}$ = 7.0 cal/deg/mole *(29.29 J/K/mol)*.

Melting point of gold = 1063°C *(1336 K)*.

Heat of fusion of gold, ΔH_f = 3,050 cal/mole *(12,761 J/mol)*.