University of Science
Department of Materials science

Chapter 6

Heat Capacity, Enthalpy, Entropy, and the Third Law of Thermodynamics

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INTRODUCTION

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.6}$$

and the heat capacity at constant pressure

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.7}$$

If E is an extensive property for per mole of the system

E' will be used to denote the value of the property for the entire system containing n moles

Eqs. (2.6) and (2.7) can thus be written equivalently as

$$dU' = C_v dT = nc_v dT \quad \text{or} \quad dU = c_v dT \tag{2.6a}$$

$$dH' = C_p dT = nc_p dT \quad \text{or} \quad dH = c_p dT \tag{2.7a}$$

$$\Delta H = H(T_2,P) - H(T_1,P) = \int_{T_1}^{T_2} c_p dT \tag{6.1}$$

THE EMPIRICAL REPRESENTATION OF HEAT CAPACITIES

The experimentally measured variation of **the constant-pressure molar heat capacity of a material with temperature** is normally fitted to an expression of the form

$$c_p = a + bT + cT^{-2}$$

For example $ZrO2$ exists as monoclinic $\alpha ZrO2$ from room temperature to 1478 K and as tetragonal βZrO_2 in the range of temperature 1478–2670 K and each polymorph has its own equation giving the variation of its heat capacity with temperature.

$$\alpha\text{-}ZrO_2 \quad c_p = 69.62 + 7.53 \times 10^{-3}T - 14.06 \times 10^{5}T^{-2}\ \text{J/K·mole}$$

over the temperature range 298–1478 K, and

$$\beta\text{-}ZrO_2 \quad c_p = 74.48\ \text{J/K·mole}$$

ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

For a closed system of fixed composition undergoing a change in temperature from T_1 to T_2 at the constant pressure P, integration of Eq. (2.7) gives Eq. (6.1):

$$\Delta H = H(T_2,P) - H(T_1,P) = \int_{T_1}^{T_2} c_p dT \tag{6.1}$$

When a system undergoes a chemical reaction or a phase transformation at constant temperature and pressure, e.g., **the reaction *A+B=AB*, Δ*H*** is the difference between the enthalpy of the products of the reaction (the state 2), and the enthalpy of the reactants (the state 1), i.e.

$$\Delta H(T,P) = H_{AB}(T,P) - [H_A(T,P) + H_B(T,P)]$$

Hess's law

$$\Delta H(T,P) = H_{AB}(T,P) - [H_A(T,P) + H_B(T,P)] \qquad (6.8)$$

Hess's law

If Δ*H* is a **positive quantity** the reaction causes the system to absorb heat from its thermos starting heat bath, and the reaction is thus ***endothermic***.
Conversely, if Δ*H* is a **negative quantity** the reaction occurs with an evolution of heat and is thus an ***exothermic*** process.

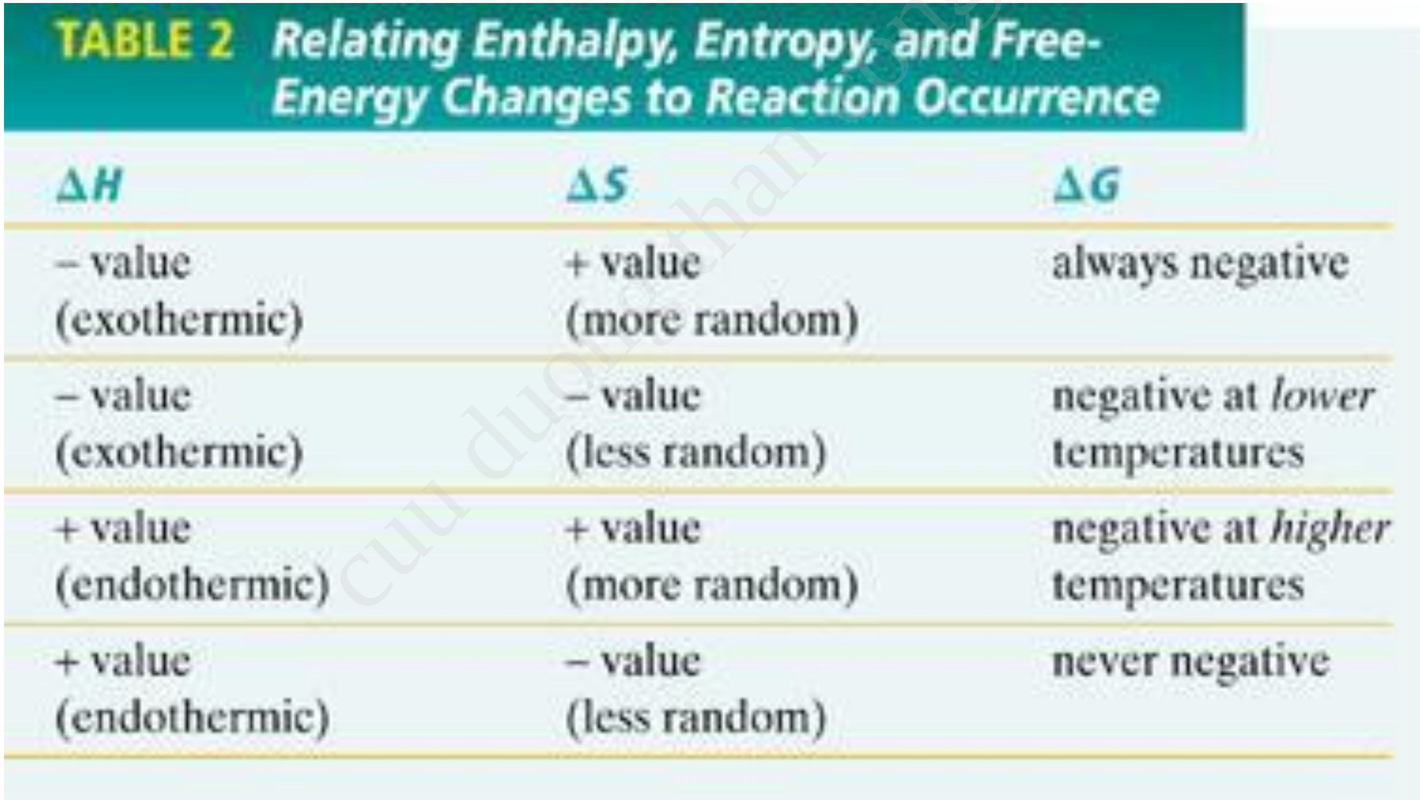


TABLE 2 ***Relating Enthalpy, Entropy, and Free-Energy Changes to Reaction Occurrence***

Δ*H*	Δ*S*	Δ*G*
– value (exothermic)	+ value (more random)	always negative
– value (exothermic)	– value (less random)	negative at *lower* temperatures
+ value (endothermic)	+ value (more random)	negative at *higher* temperatures
+ value (endothermic)	– value (less random)	never negative

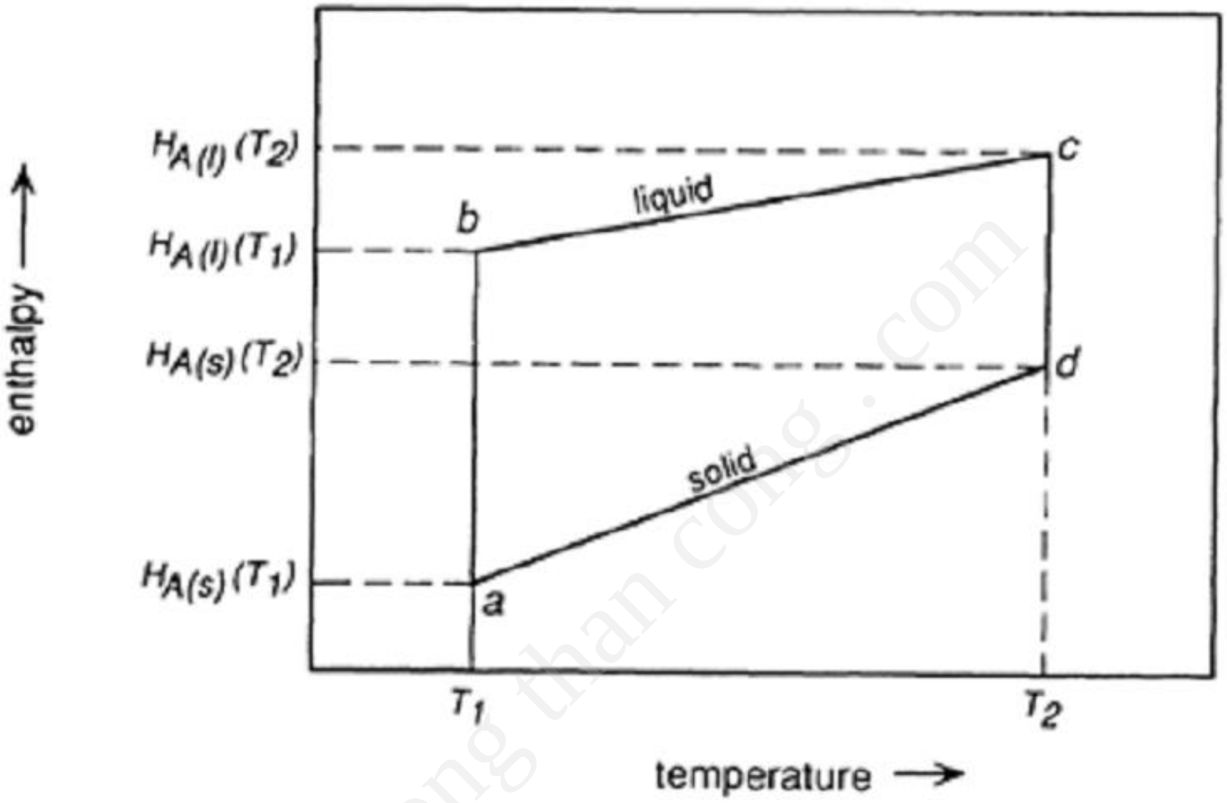


Figure 6.6 The variation, with temperature, of the molar enthalpies of the solid and liquid phases of a substance.

$$A_{(s)} \rightarrow A_{(l)}$$

i.e., the melting of pure *A*. ΔH_{T1} for this process is the difference between the molar enthalpies of liquid and solid *A* at the temperature T_1:

$$\Delta H_{T_1} = H_{A(l)}(T_1) - H_{A(s)}(T_1)$$

This change in enthalpy is represented by line *ba* in Fig. 6.6.

For the change of phase occurring at the temperature *T*2

$$\Delta H_{T_2} = H_{A(l)}(T_2) - H_{A(s)}(T_2)$$

which is represented in Fig. 6.6 by the line of *cd*. As *H* is a state function, then

$$\Delta H(a \rightarrow b) = \Delta H(a \rightarrow d) + \Delta H(d \rightarrow c) + \Delta H(c \rightarrow b) \qquad \text{(i)}$$

where $\Delta H(a \rightarrow d)$ is the heat required to increase the temperature of one mole of solid *A* from T_1 to T_2 at constant pressure.

$$= \int_{T_1}^{T_2} c_{p_{A(s)}} dT$$

in which $d_{pA(s)}$ is the molar heat capacity of solid *A*

$$\Delta H(d \rightarrow c) = \Delta H_{T_2}$$

$\Delta H(c \rightarrow b)$ is the heat which is evolved by 1 mole of liquid A when its temperature is decreased from T_2 to T_1 (or the negative of the amount of heat required to raise the temperature of a mole of liquid A from T_1 to T_2)

$$\int_{T_2}^{T_1} c_{p_{A(l)}} dT = -\int_{T_1}^{T_2} c_{p_{A(l)}} dT$$

in which $C_{pA(l)}$ is the molar heat capacity of liquid A. Substitution of the individual expressions into Eq. (i) gives

$$\Delta H(A_{(s)} \rightarrow A_{(l)} \text{ at } T_1) = \Delta H(A_{(s)} \rightarrow A_{(l)} \text{ at } T_2) + \int_{T_1}^{T_2} c_{p_{A(s)}} dT - \int_{T_1}^{T_2} c_{p_{A(l)}} dT$$

or

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta c_p dT \qquad (6.9)$$

where

$$\Delta c_p = c_{p_{A(l)}} - c_{p_{A(s)}}$$

ENTHALPY AND HESS' LAW

Ex #1

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^\circ = ?$

$$C_{(s)} + \tfrac{1}{2} O_{2(g)} \rightarrow \cancel{CO_{(g)}} \qquad \Delta H^\circ = -110.5\ \text{kJ}$$

$$\cancel{CO_{(g)}} + \tfrac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -283.0\ \text{kJ}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5\ \text{kJ}$$

The enthalpies are added together

Therefore the enthalpy is -393.5 kJ

THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

For a closed system undergoing a reversible process, the Second Law gives

$$dS = \frac{\delta q}{T} \tag{3.8}$$

If the process is conducted at constant pressure, then

$$dS = \left(\frac{\delta q}{T}\right)_p = \left(\frac{dH}{T}\right)_p = c_p \frac{dT}{T}$$

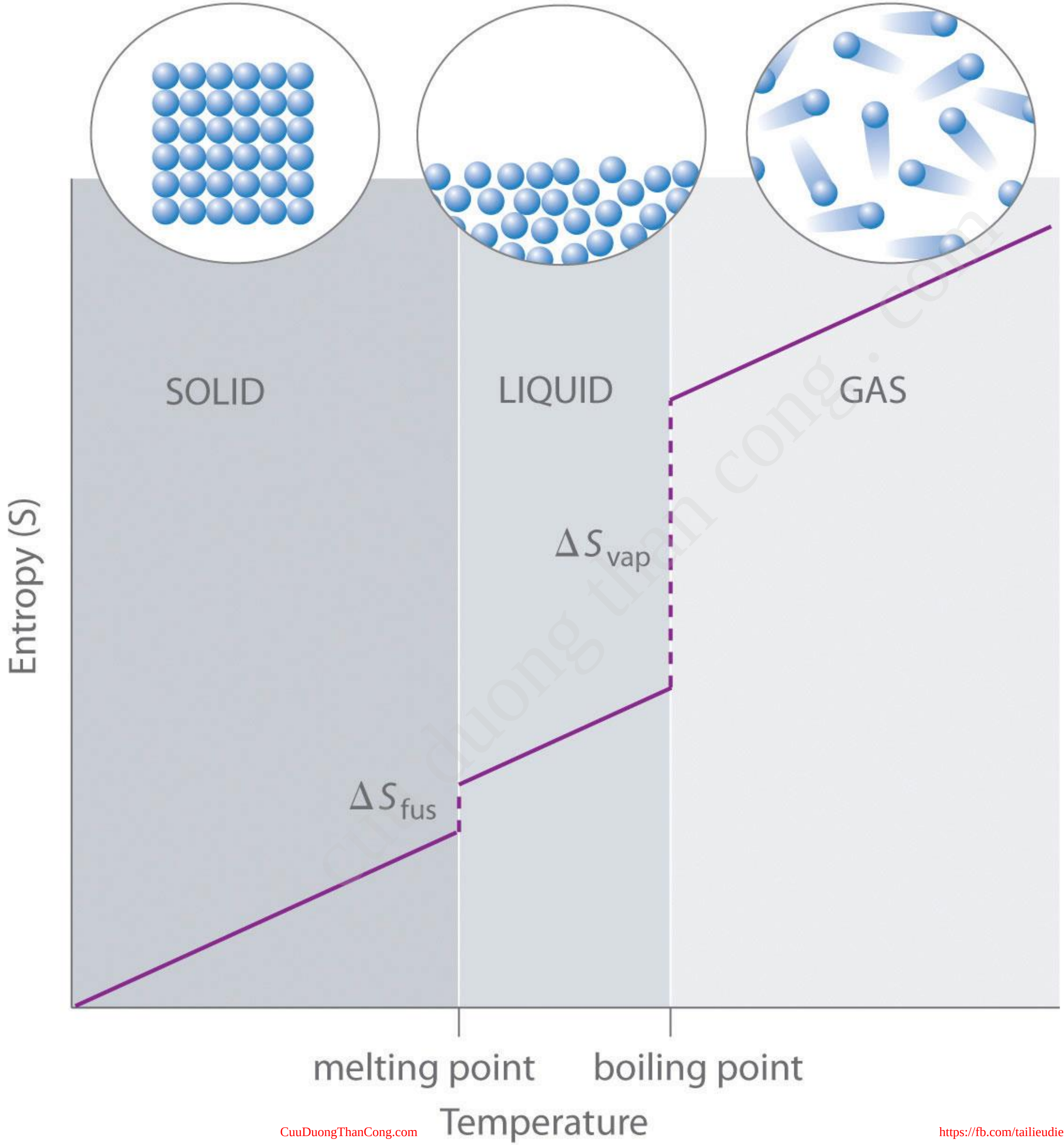
and thus if the temperature of a closed system of fixed composition is increased from T_1 to T_2 at constant pressure, the increase in the entropy per mole of the system, ΔS, is given by

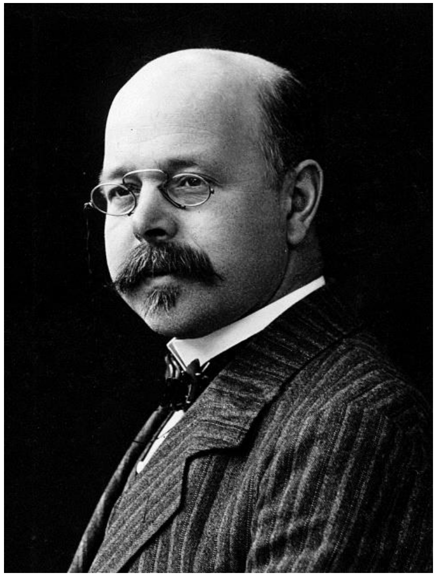
$$\Delta S = S(T_2,P) - S(T_1,P) = \int_{T_1}^{T_2} \frac{c_p}{T}\, dT \qquad (6.12)$$

This change of entropy is obtained the area under a plot of C_p/T vs. T between the limits T_2 and T_1, or, equivalently, as the area under a plot of C_p vs. In T between the limits In T_2 and In T_1. Generally, S_T, the molar entropy of the system at any temperature T is given by

$$S_T = S_0 + \int_0^T \frac{c_p}{T}\, dT \qquad (6.13)$$

where S_0 is the molar entropy of the system at 0 K. Consideration of the value of S_0 leads to the statement of what is commonly called the **Third Law of Thermodynamics.**


SOLID
LIQUID
GAS
Entropy (S)
ΔS_{vap}
ΔS_{fus}
melting point
boiling point
Temperature



In 1906 **Nernst postulated that**, for chemical reactions between pure solids or pure liquids, the terms

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial \Delta H}{\partial T}\right)_P$$

approach zero as temperature approaches absolute zero. For any change in the state of a system, e.g., a chemical reaction at the constant temperature T, Eq. (5.2) gives

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

and thus Nernst's postulate is that ΔG for the reaction varies with temperature as shown in *Fig. 6.10*

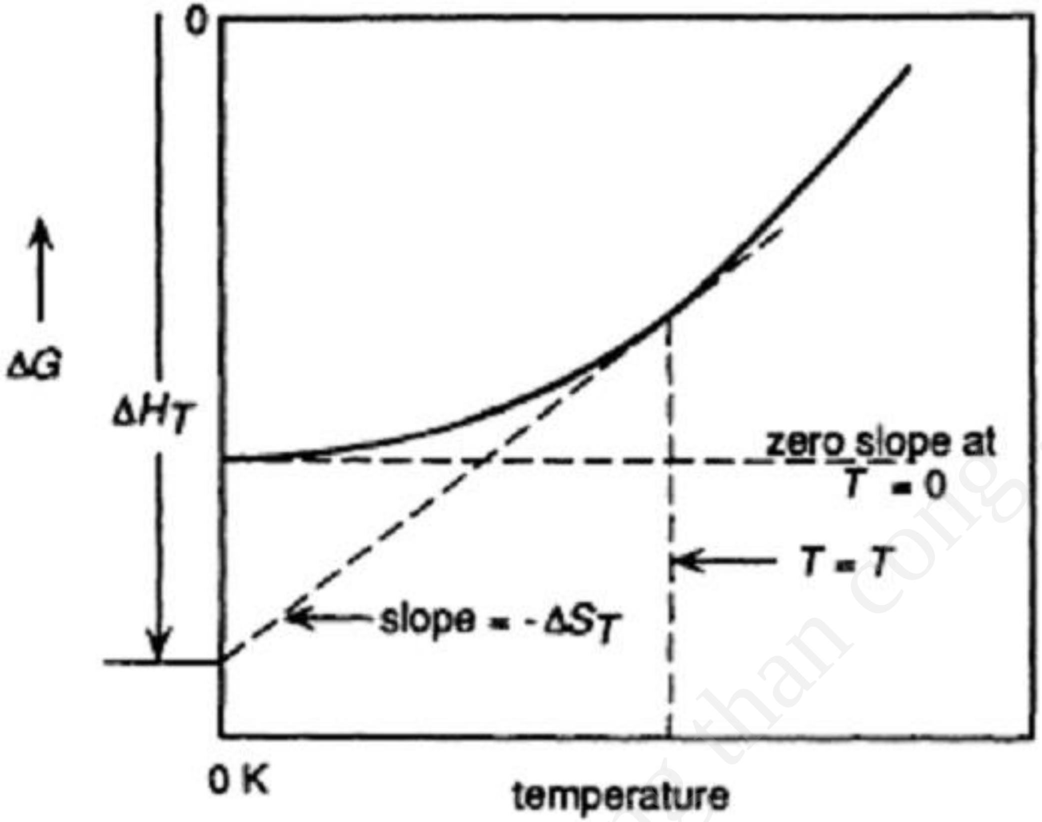


Figure 6.10 The variation of the change in the Gibbs free energy for a reaction with temperature as the temperature approaches absolute zero.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S$$

From Eq. (5.12)

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

and thus

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P = \Delta c_p$$

Nernst’s heat theorem states that **“for all reactions involving substances in the condensed state, ΔS is zero at the absolute zero of temperature**.” Thus, for the general reaction

$$A + B = AB$$

$\Delta S = S_{AB} - S_A - S_B = 0$ at $T = 0$, and if S_A and S_B are assigned the value of zero at 0 K, then the compound AB also has zero entropy at 0 K.

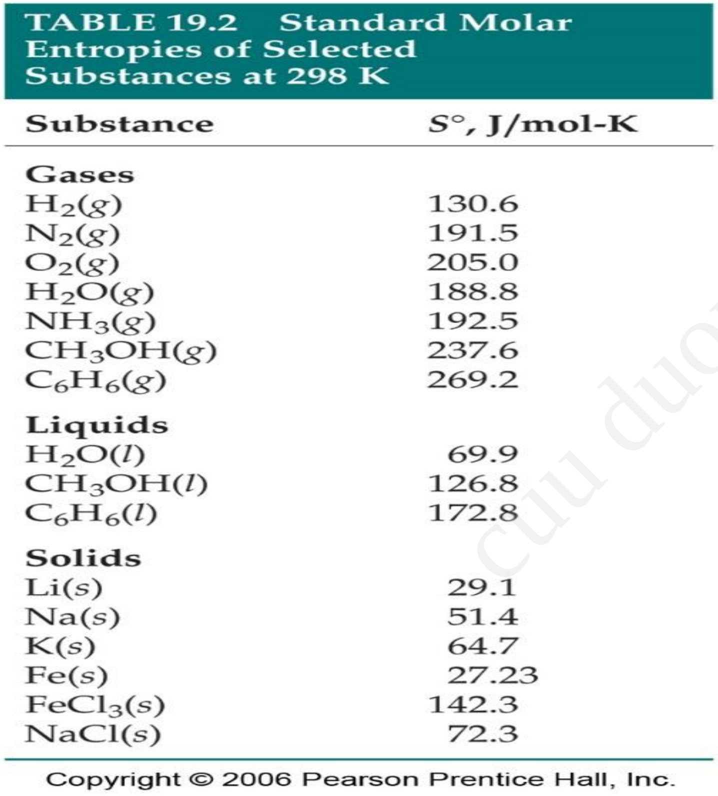
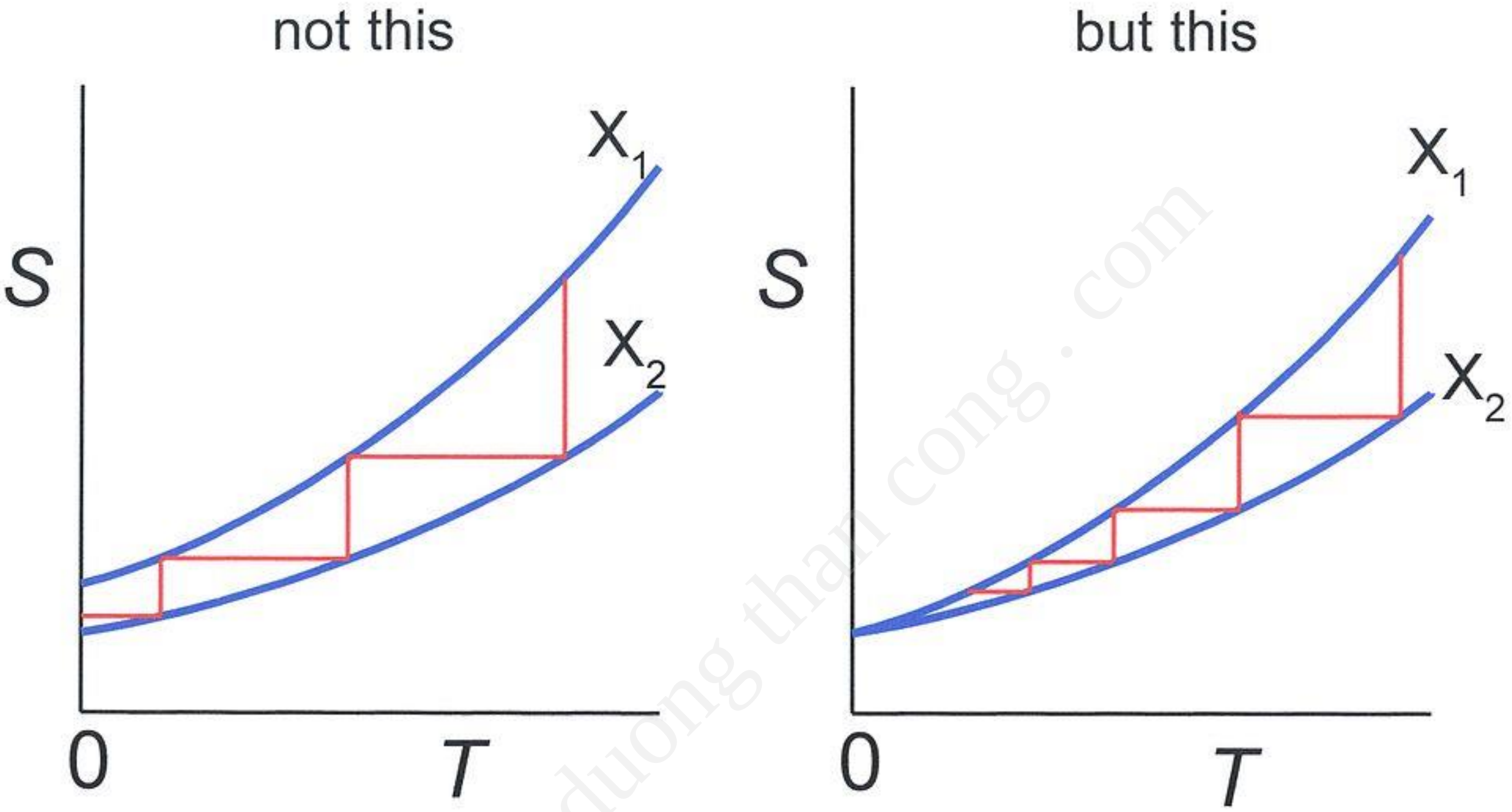


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

The Third Law of Thermodynamics defines zero entropy: The entropy of a perfectly ordered crystalline solid at 0K is 0. Under all other circumstances, absolute entropies are positive.



Left side: Absolute zero can be reached in a finite number of steps if$S(0,X_1) \neq S(0, X_2)$. Right: An infinite number of steps is needed since $S(0,X_1)=S(0,X_2)$.

EXPERIMENTAL VERIFICATION OF THE THIRD LAW

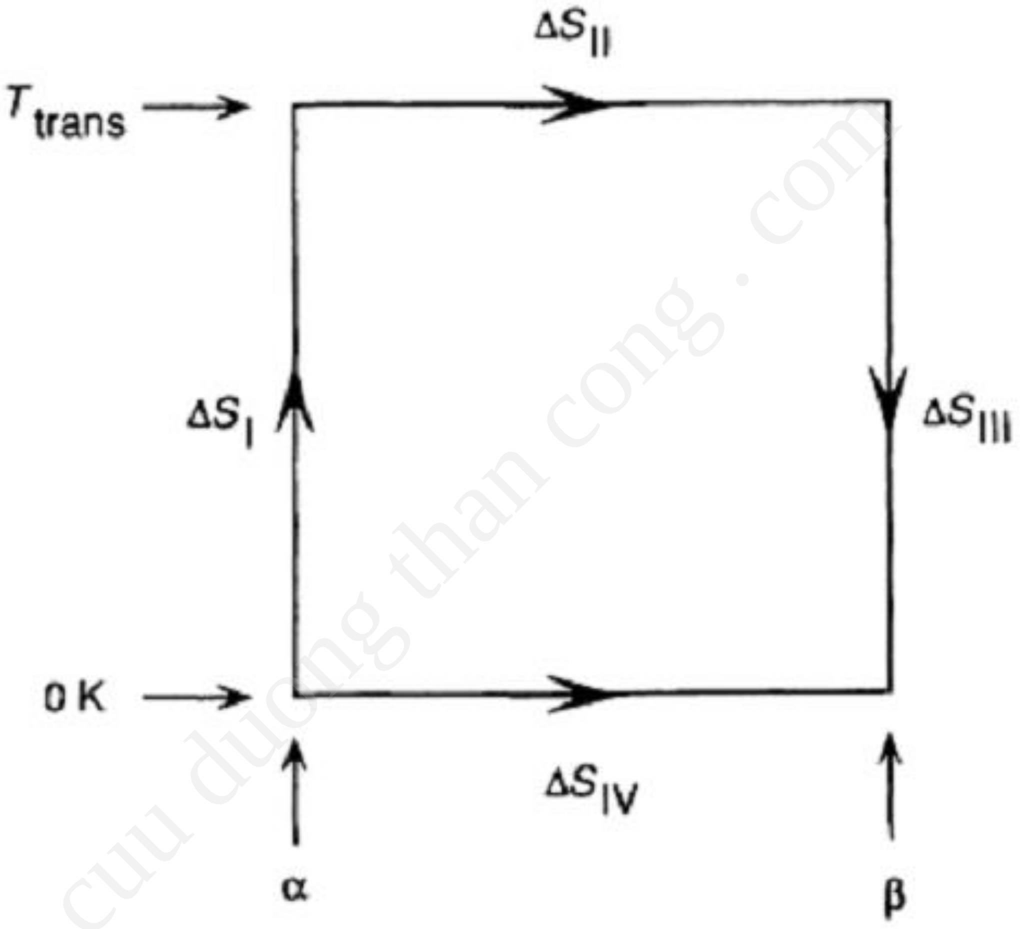


Figure 6.11 The cycle used for the experimental verification of the Third Law of Thermodynamics.

The Third Law can be verified by considering a phase transition in an element such as

$$\alpha \rightarrow \beta$$

where α and β are allotropes of the element. In Fig. 6.11 T_{trans} is the temperature, at atmospheric pressure, at which the α and β phases are in equilibrium with one another. For the cycle shown in Fig. 6.11

$$\Delta S_{\text{IV}} = \Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}}$$

For the Third Law to be obeyed, $\Delta S_{\text{IV}}=0$, which requires that

$$\Delta S_{\text{II}} = -(\Delta S_{\text{I}} + \Delta S_{\text{III}})$$

where

$$\Delta S_{\text{I}} = \int_0^{T_{\text{trans}}} \frac{c_{p(\alpha)}}{T}\, dT$$

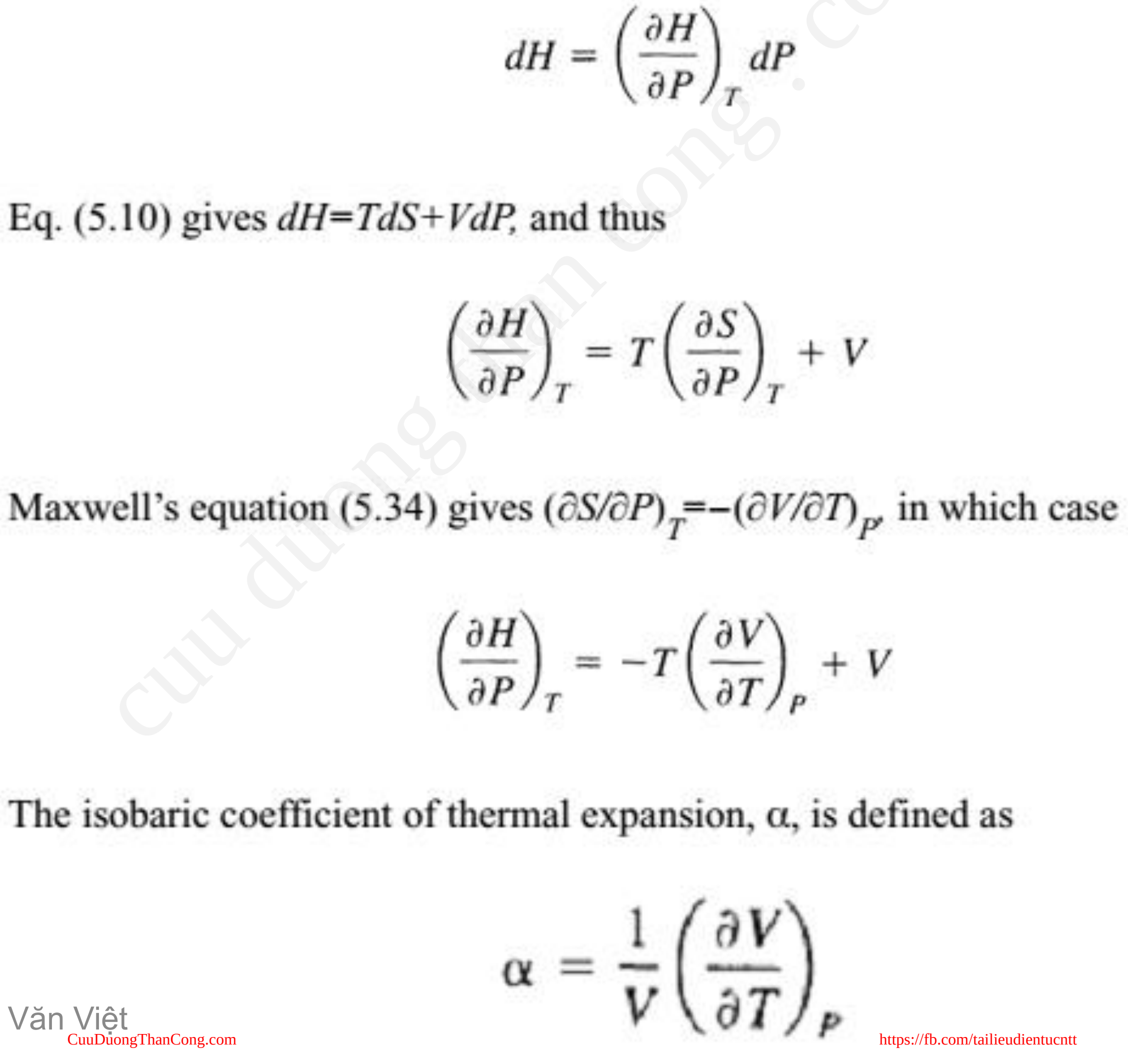
$$\Delta S_{\text{II}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}$$

$$\Delta S_{\text{III}} = \int_{T_{\text{trans}}}^{0} \frac{c_{p(\beta)}}{T}\, dT$$

ΔS_{II}, which is called the experimental entropy change, and $-(\Delta S_{\text{I}}+\Delta S_{\text{III}})$, which is called the Third Law entropy change, are equal to one another if the Third Law is obeyed.

THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

For a closed system of fixed composition undergoing a change of pressure at constant temperature.



$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP$$

Eq. (5.10) gives $dH = TdS + VdP$, and thus

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Maxwell's equation (5.34) gives $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, in which case

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

The isobaric coefficient of thermal expansion, α, is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and thus

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\alpha V + V = V(1 - \alpha T)$$

The change in molar enthalpy caused by the change in state from (P_1, T) to (P_2, T) is thus

$$\Delta H = H(P_2,T) - H(P_1,T) = \int_{P_1}^{P_2} V(1 - \alpha T)dP \qquad (6.14)$$

For an ideal gas, $\alpha = 1/T$, and thus Eq. (6.14) shows again that the enthalpy of an ideal gas is independent of pressure.

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The molar volume and expansivity of Fe are, respectively, 7.1 cm^3 and $0.3 \times 10^{-4}\ \text{K}^{-1}$. Thus an increase in the pressure exerted on Fe from 1 to 100 atm at 298 K causes the molar enthalpy to increase by

$$\begin{aligned} 7.1 \times 10^{-3} \times (1 - 0.3 \times 10^{-4} \times 298) \times (100 - 1) &= 0.696\ \text{liter}\cdot\text{atm} \\ &= 0.696 \times 101.3 = 71\ \text{J} \end{aligned}$$

The same increase in molar enthalpy would be obtained by heating Fe from 298 to 301 K at 1 atm pressure.

For a closed system of fixed composition undergoing a change of pressure at constant temperature,

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP$$

Maxwell's equation (5.34) is $(\partial S/\partial P)_T = -(\partial V/\partial T)_p$ which, with the definition of α, gives

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

Thus, for the change of state (P_1, T) to (P_2, T)

$$\Delta S = S(P_2,T) - S(P_1,T) = -\int_{P_1}^{P_2} \alpha V dP \qquad (6.15)$$

For an ideal gas, as $\alpha = 1/T$, Eq. (6.15) simplifies to

$$\Delta S = -\int_{P_1}^{P_2} Rd\ln P = -R\ln\left(\frac{P_2}{P_1}\right) = R\ln\left(\frac{V_2}{V_1}\right)$$

For a closed system of fixed composition undergoing changes in both pressure and temperature, combination of Eqs. (6.1) and (6.14) gives

$$\Delta H = H(P_2,T_2) - H(P_1,T_1) = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} V(1 - \alpha T)dP \qquad (6.16)$$

and combination of Eqs. (6.12) and (6.15) gives

$$\Delta S = S(P_2,T_2) - S(P_1,T_1) = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \alpha V dP \qquad (6.17)$$

Just as it was required that the temperature dependence of C_p be known for integration of Eqs. (6.1) and (6.13), strictly, it is required that the pressure dependence of V and α be known for integration of Eqs. (6.14) and (6.15). However, for condensed phases being considered over small ranges of pressure, these pressure dependencies can be ignored.

Home works
From 6.1 to 6.10, page 171 and 172, David Gaskell

The END