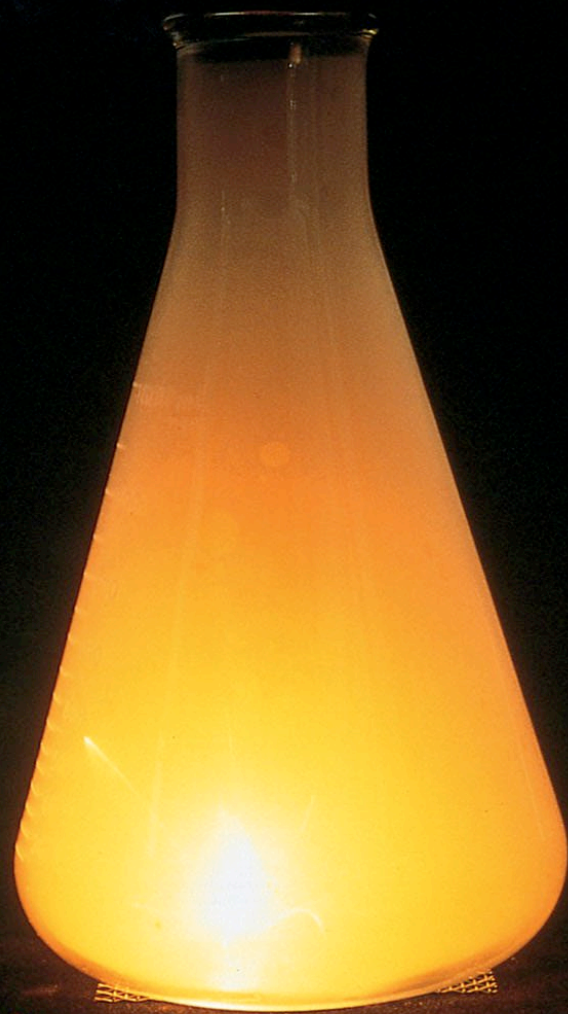


13

CHAPTER

SPONTANEOUS PROCESSES AND
THERMODYNAMIC EQUILIBRIUM

- 13.1** The Nature of Spontaneous Processes
- 13.2** Entropy and Spontaneity:
A Molecular Statistical Interpretation
- 13.3** Entropy and Heat: Macroscopic Basis of the
Second Law of Thermodynamics
- 13.4** Entropy Changes in Reversible Processes
- 13.5** Entropy Changes and Spontaneity
- 13.6** The Third Law of Thermodynamics
- 13.7** The Gibbs Free Energy



Spontaneous reaction

The reaction of solid sodium with chlorine gas proceeds imperceptibly, if at all, until the addition of a drop of water sets it off.

13.1 THE NATURE OF SPONTANEOUS PROCESSES

◆ First Law of Thermodynamics

~ Cannot predict the **directionality** of spontaneous processes.

◆ Second Law of Thermodynamics

➤ Entropy, S

$\Delta S_{\text{universe}} > 0$ for a spontaneous process

➤ Gibbs free energy, G

$\Delta G_{\text{system}} < 0$ for a spontaneous process at constant P and T

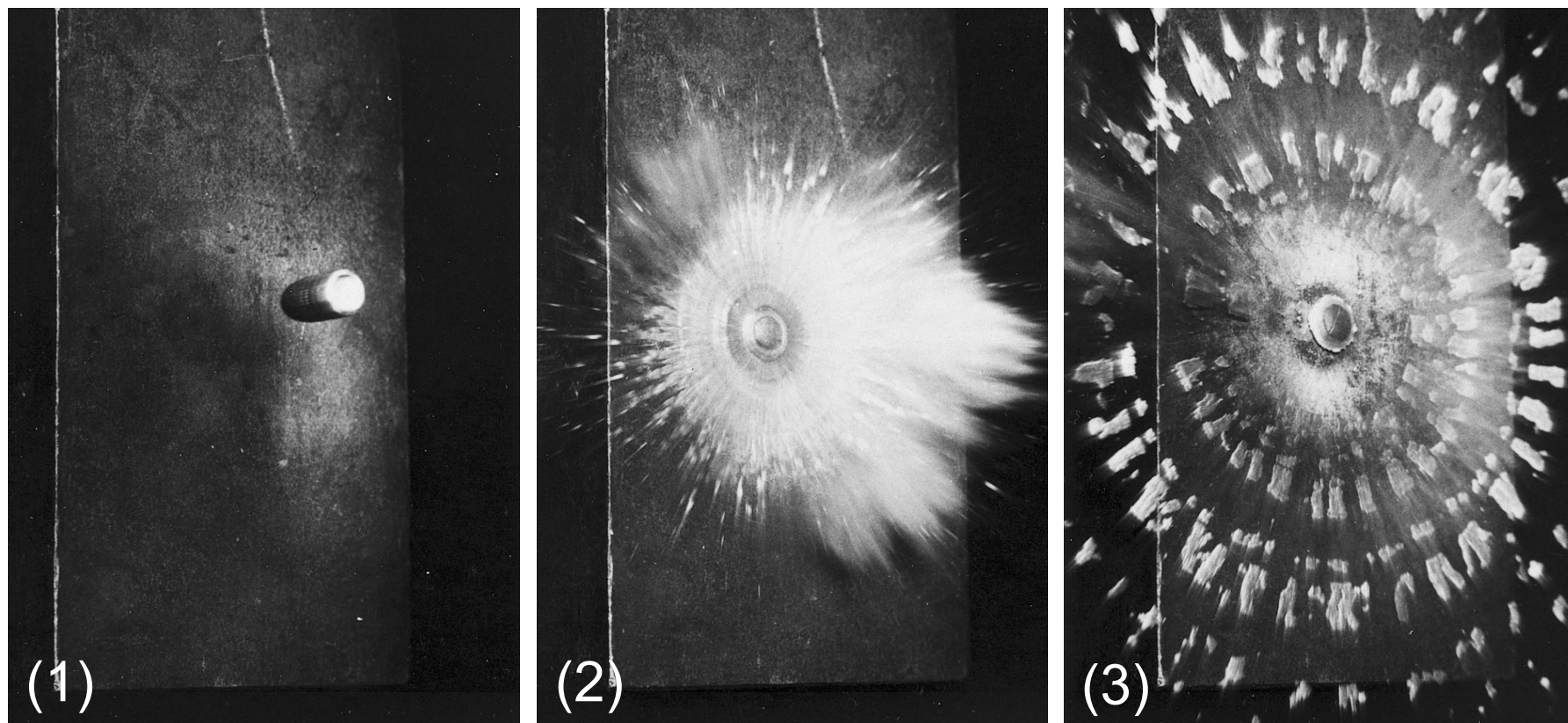
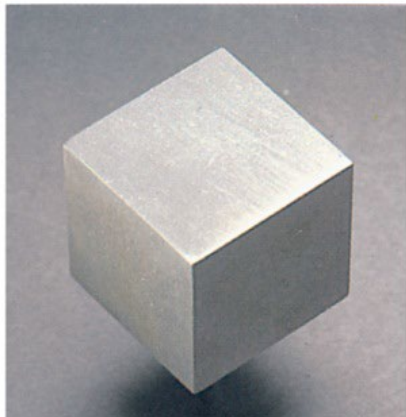


Fig. 13.1 A bullet is hitting a steel plate: (1) \rightarrow (2) \rightarrow (3).
The reverse process is exceedingly unlikely.

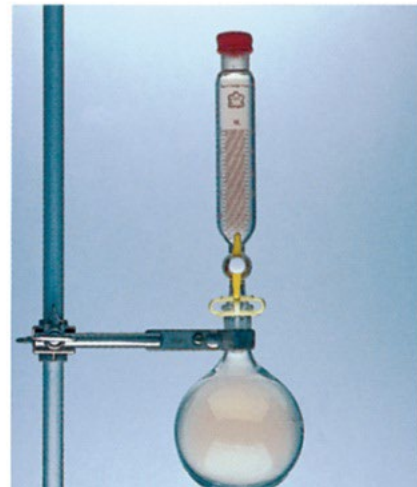
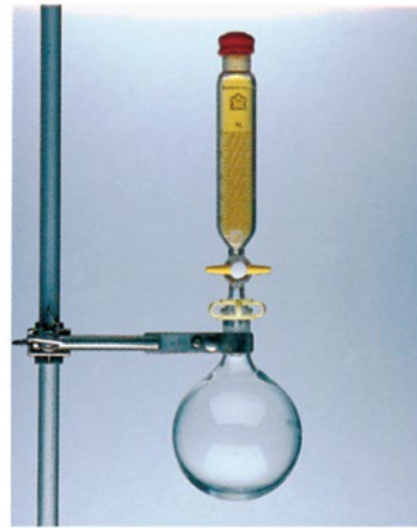
hot



cold



Expansion
of a gas



- Thermodynamics determines whether a reaction is possible, whereas chemical kinetics determines whether it is practical.
- The direction of each of these spontaneous processes is readily apparent by observing the initial and final states, regardless of their paths (state function)



13.2 ENTROPY AND SPONTANEITY: A MOLECULAR STATISTICAL INTERPRETATION

➤ Free adiabatic expansion

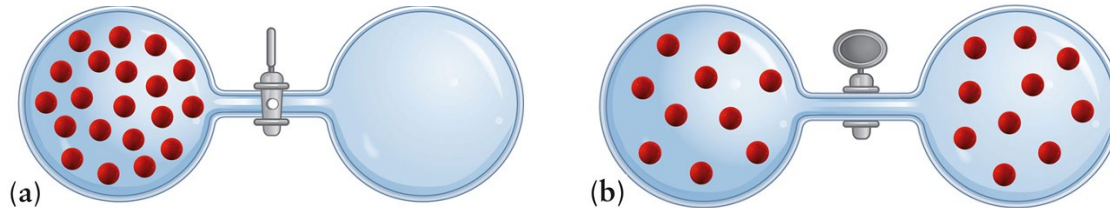


Fig. 13.2 Free expansion of a gas into a vacuum. The half of the gas is found in each bulb, at equilibrium, after the stopcock is opened.

❖ Distribution of 2 molecules

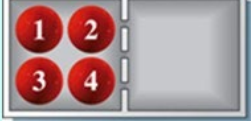








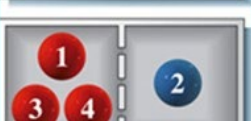


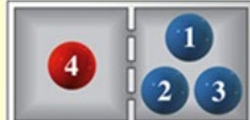
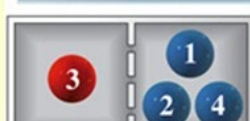


$$(N_L=2, N_R=0) \text{ or } (N_L=0, N_R=2)$$

$$\text{Probability (P)} = {}_2C_0 \times \left(\frac{1}{2}\right)^2 = \frac{2!}{(0!)(2!)} \times \frac{1}{4} = \frac{1}{4}$$

$$(N_L=1, N_R=1)$$

$$\text{Probability (P)} = {}_2C_1 \times \left(\frac{1}{2}\right)^2 = \frac{2!}{(1!)(1!)} \times \frac{1}{4} = \frac{2}{4}$$

❖ Distribution of 4 molecules

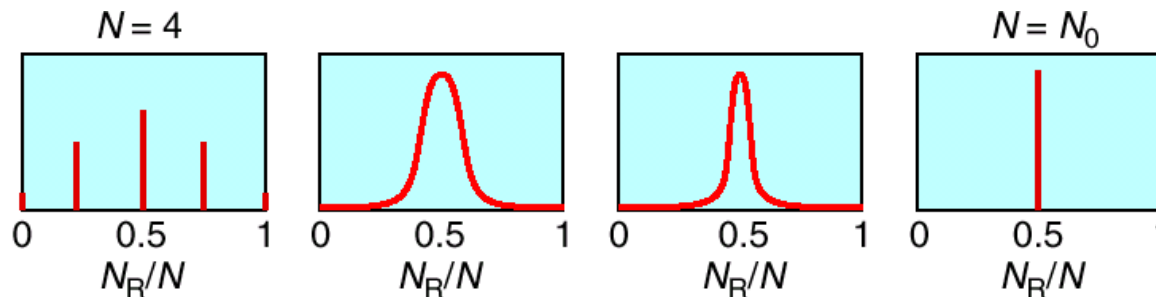
<p>$(N_L=4, N_R=0)$ or $(N_L=0, N_R=4)$</p> $P = {}_4C_0 \times \left(\frac{1}{2}\right)^4 = \frac{4!}{(0!)(4!)} \times \frac{1}{16} = \frac{1}{16}$		
<p>$(N_L=2, N_R=2)$</p> $P = {}_4C_2 \times \left(\frac{1}{2}\right)^4 = \frac{4!}{(2!)(2!)} \times \frac{1}{16} = \frac{6}{16}$	  	  
<p>$(N_L=3, N_R=1)$ or $(N_L=1, N_R=3)$</p> $P = {}_4C_1 \times \left(\frac{1}{2}\right)^4 = \frac{4!}{(1!)(3!)} \times \frac{1}{16} = \frac{4}{16}$	   	   

→ The directionality of spontaneous change is a consequence of the large numbers of molecules in the macroscopic systems treated by thermodynamics.

❖ Distribution of $N_A = 6.0 \times 10^{23}$ molecules (1 mol)

$(N_L = N_A, N_R = 0)$ or $(N_L = 0, N_R = N_A)$

$$\text{Probability} = {}_{N_A} C_0 \times \left(\frac{1}{2}\right)^{N_A} = \left(\frac{1}{2}\right)^{6 \times 10^{23}} = \left(\frac{1}{10}\right)^{1.8 \times 10^{23}} \rightarrow 0$$



$$\text{Statistical fluctuation: } \frac{\Delta N}{N} = O\left(\frac{1}{\sqrt{N}}\right) \longrightarrow 0 \text{ as } N \rightarrow \infty$$

Random, statistical behavior of a **large** number of particles
→ Directionality of spontaneous change

→ the range of possible motions (that is, the range of possible positions and momenta) available to the molecules while the system is held in that particular thermodynamic state.

◆ Entropy and Molecular Motions

➤ Microstate

~ Microscopic, mechanical states available to N molecules in the system

➤ Number of microstates, $\Omega(E, V, N)$

~ Increasing the volume

→ increasing available values of position

→ increasing $\Omega(E, V, N)$

➤ Entropy, S (J/K)

~ Measure of the number of available microstates

❖ Boltzmann's *statistical definition of entropy*

$$S = k_B \ln \Omega(E, V, N)$$

➤ Free expansion of a gas

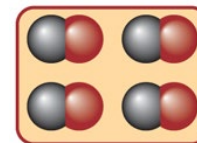
Spontaneous process ~ increasing $\Omega(E, V, N)$ ~ increasing S

EXAMPLE 8.7

Calculate the entropy of a tiny solid made up of four diatomic molecules of a compound such as carbon monoxide, CO, at $T = 0$ when (a) the four molecules have formed a **perfectly ordered** crystal in which all molecules are aligned with their C atoms on the left and (b) the four molecules lie in **random orientations, but parallel**.

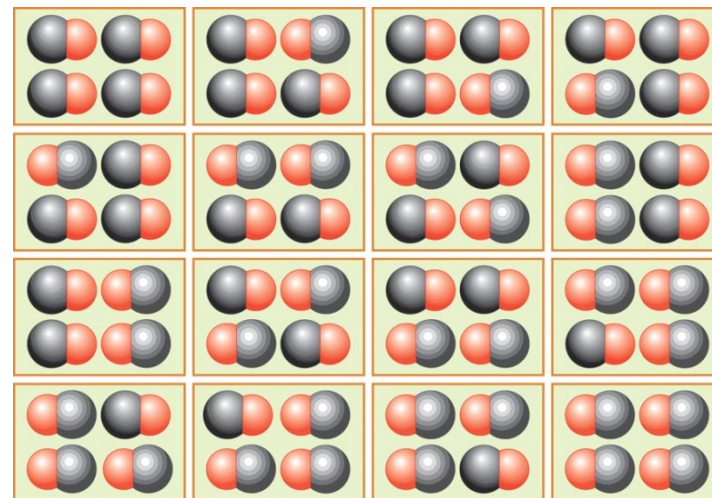
(a) 4 CO molecules **perfectly ordered**:

$$S = k_B \ln 1 = 0$$



(b) 4 CO in **random, but parallel**:

$$S = k_B \ln 2^4 = 3.8281 \times 10^{-23} \text{ J/K}$$



(c) 1 mol CO in **random, but parallel**:

$$S = k_B \ln 2^{N_A} = N_A k_B \ln 2 = 5.76 \text{ J/K}$$

EXAMPLE 13.3 Free expansion of 1 mol of a gas from $V/2$ to V . $\Delta S = ?$

Number of states available per molecule = cV

Number of states available for N -molecules system = $\Omega = (cV)^N$

Entropy is an **extensive** quantity, $S = S(\Omega) = S[(cV)^N] \propto N$

$$\Rightarrow S \propto \ln \Omega$$

$$\Delta S = N_0 k_B \ln (cV) - N_0 k_B \ln (cV/2) = N_0 k_B \ln 2 > 0$$

❖ Entropy and Disorder

Ordered state \rightarrow Disordered state : $\Delta S_{\text{sys}} > 0$

gas expansion, melting, boiling, diffusion, ...

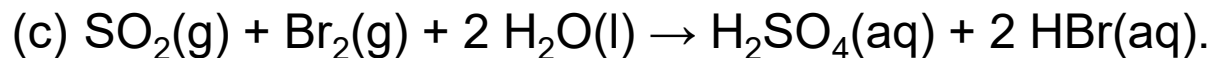
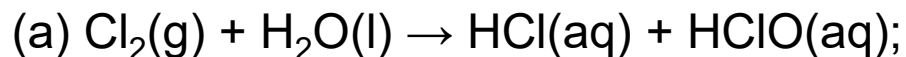
Entropy is a measure of **disorder (randomness)**.

8.31 List the following substances in order of increasing molar entropy at 298 K: $\text{H}_2\text{O}(\text{l})$, $\text{H}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{s})$, $\text{C}(\text{s}, \text{diamond})$. Explain your reasoning.

8.31 It is easy to order H_2O in its various phases because entropy will increase when going from a solid to a liquid to a gas. The main question concerns where to place $\text{C}(\text{s}, \text{diamond})$ in this order, and that will essentially become a question of whether $\text{C}(\text{s}, \text{diamond})$ should have more or less entropy than $\text{H}_2\text{O}(\text{s})$, because we would automatically expect $\text{C}(\text{s}, \text{diamond})$ to have less entropy than any liquid. Because water is a molecular substance held together in the solid phase by weak hydrogen bonds, and in $\text{C}(\text{s}, \text{diamond})$ the carbon is more rigidly held in place and will have less entropy.

In summary, $\text{C}(\text{s}, \text{diamond}) < \text{H}_2\text{O}(\text{s}) < \text{H}_2\text{O}(\text{l}) < \text{H}_2\text{O}(\text{g})$.

8.35 Without performing any calculations, predict whether there is an increase or a decrease in entropy for each of the following processes:



8.35 (a) Entropy should decrease because the number of moles of gas is less on the product side of the reaction.

(b) Entropy should increase because the dissolution of the solid copper phosphate will increase the randomness of the copper and phosphate ions.

(c) Entropy should decrease as the total number of moles decreases.

→ defines the entropy function in terms of measurable macroscopic quantities, providing a means to calculate the changes in entropy caused by specific processes.

13.3 ENTROPY AND HEAT: MACROSCOPIC BASIS OF THE SECOND LAW OF THERMODYNAMICS

◆ Background of the Second Law of Thermodynamics

➤ Efficiency of heat engines

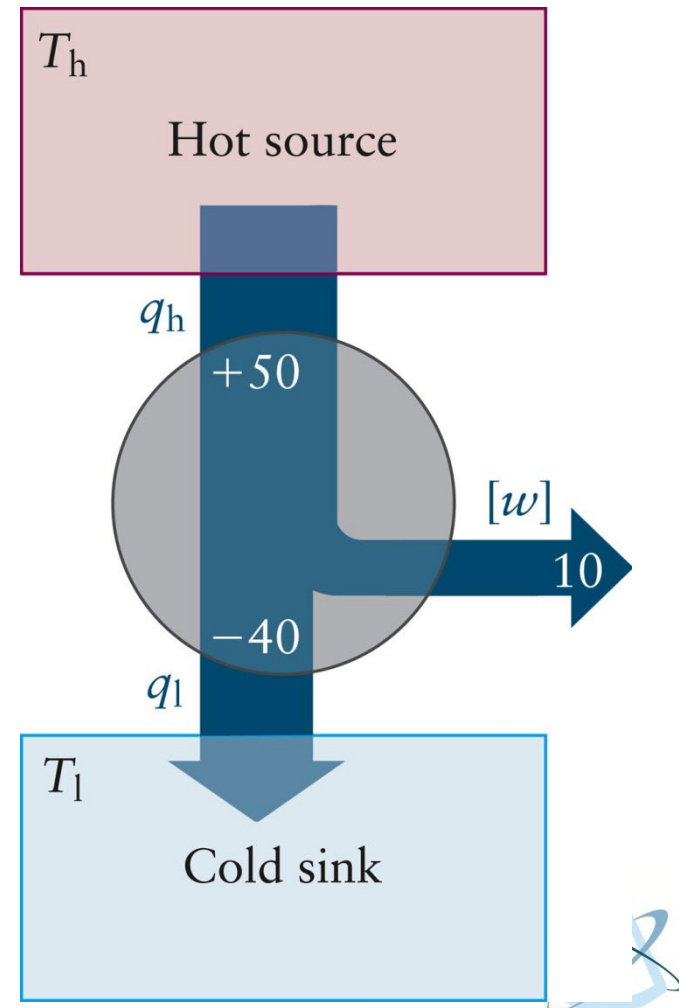
heat \Rightarrow work

➤ Thermodynamic efficiency of the Carnot cycle

$$\varepsilon = \frac{w}{q_h} = 1 - \frac{T_l}{T_h}$$

→ fundamental limit of an engine

General Chemistry I



◆ Equivalent Formulations of the Second Law of Thermodynamics

➤ Rudolf Clausius

*There is no device that can transfer heat from a **colder** to **warmer** reservoir without net expenditure of work.*

➤ Lord Kelvin

*There is no device that can transfer heat withdrawn from a reservoir **completely** into work with no other effect.*

→ a bold extrapolation of the results of a great deal of direct experimental observation under controlled conditions.

◆ Thermodynamic Definition of Entropy

➤ Carnot's analysis

Efficiency for a **reversible heat engine cycle**

➤ Clausius's analysis of Carnot's work

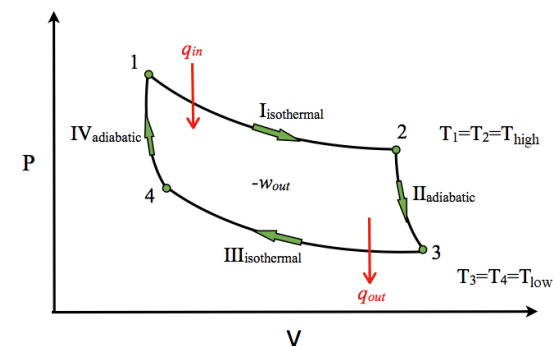
$$\frac{q_h}{T_h} + \frac{q_l}{T_l} = 0 \quad \rightarrow \quad \frac{q}{T} \text{ is a state function}$$

→ Because the sum of its changes in a cyclic process is zero

$\int \frac{dq_{\text{rev}}}{T}$: independent of path in *any* reversible process (state function)

$$\Delta S = S_f - S_i = \int_i^f \frac{dq_{\text{rev}}}{T}$$

→ Clausius's thermodynamic definition of entropy



13.4 ENTROPY CHANGES IN REVERSIBLE PROCESSES

◆ ΔS_{sys} for Isothermal Processes

➤ *Compression / Expansion of an ideal gas*

$$q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

$\Delta U = 0$, $w = -q$ **isothermal** process

➤ *Phase Transitions*

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T_f} = \frac{\Delta H_{\text{fus}}}{T_f}$$

❖ Trouton's rule

$\Delta S_{\text{vap}} = 88 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ for most liquids

Exception: Water, $\Delta S_{\text{vap}} = 109 \text{ J K}^{-1} \text{ mol}^{-1}$

~ ordering due to hydrogen bonds

Liquid	Boiling point (K)	$\Delta S_{\text{vap}}^{\circ}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
acetone	329.4	88.3
ammonia	239.7	97.6
argon	87.3	74
benzene	353.2	87.2
ethanol	351.5	124
helium	4.22	20.
mercury	629.7	94.2
methane	111.7	73
methanol	337.8	105
water	373.2	109

*The normal boiling point is the boiling temperature at 1 atm.

◆ ΔS_{sys} for Processes with Changing Temperature

$$\Delta S \equiv \int_{\mathbf{A}}^{\mathbf{B}} \frac{dq_{\text{rev}}}{T}$$

For a reversible **adiabatic** process ($q = 0$), $\Delta S = 0$. (**isentropic**)

For a reversible **isochoric** process, $dq_{\text{rev}} = nC_V dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} dq_{\text{rev}} = \int_{T_1}^{T_2} \frac{nC_V}{T} dT = nC_V \ln \left(\frac{T_2}{T_1} \right) \quad (\text{Const } V)$$

For a reversible **isobaric** process, $dq_{\text{rev}} = nC_P dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} dq_{\text{rev}} = \int_{T_1}^{T_2} \frac{nC_P}{T} dT = nC_P \ln \left(\frac{T_2}{T_1} \right) \quad (\text{Const } P)$$

EXAMPLE 13.5

(a) 5.00 mol argon expands reversibly at a constant $T = 298 \text{ K}$ from a $P = 10.0$ to 1.00 atm . $\Delta S = ?$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left(\frac{P_1}{P_2} \right) = +95.7 \text{ J K}^{-1}$$

(b) 5.00 mol argon expands reversibly and adiabatically at an initial $T = 298 \text{ K}$ from a $P = 10.0$ to 1.00 atm . Then the gas is heated at constant P back to 298 K . $\Delta S = ?$

For the first adiabatic process, $\Delta S = 0$; $T \rightarrow 119 \text{ K}$ (Ex 12.11)

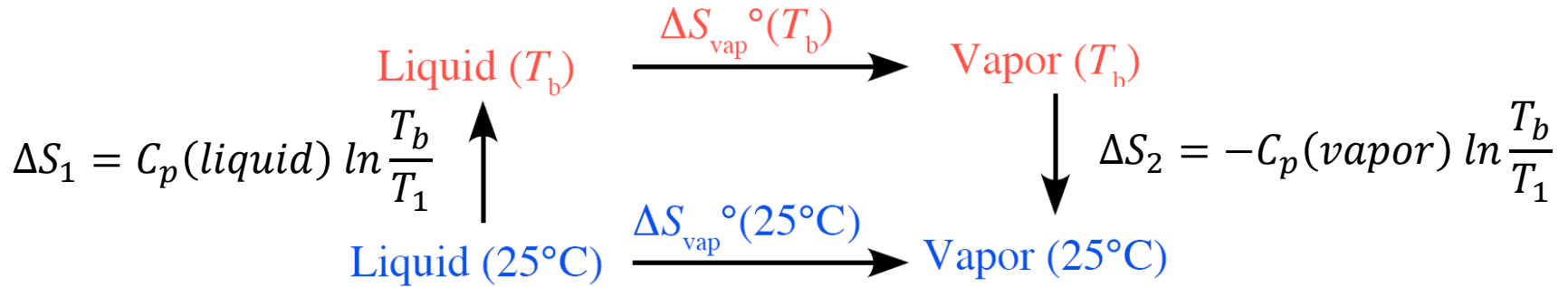
$$\text{For the second, } \Delta S = nC_P \ln \left(\frac{T_2}{T_1} \right) = n \left(\frac{5}{2} R \right) \ln \left(\frac{T_2}{T_1} \right) = +95.7 \text{ J K}^{-1}$$

➤ **Temperature dependence of $\Delta S_{\text{vap}}^\circ$**

- For the entropy of vaporization of water at 25 °C,
Heat the liquid to T_b ; allow it to vaporize; cool the vapor to 25 °C.

For 1 mol of gas,

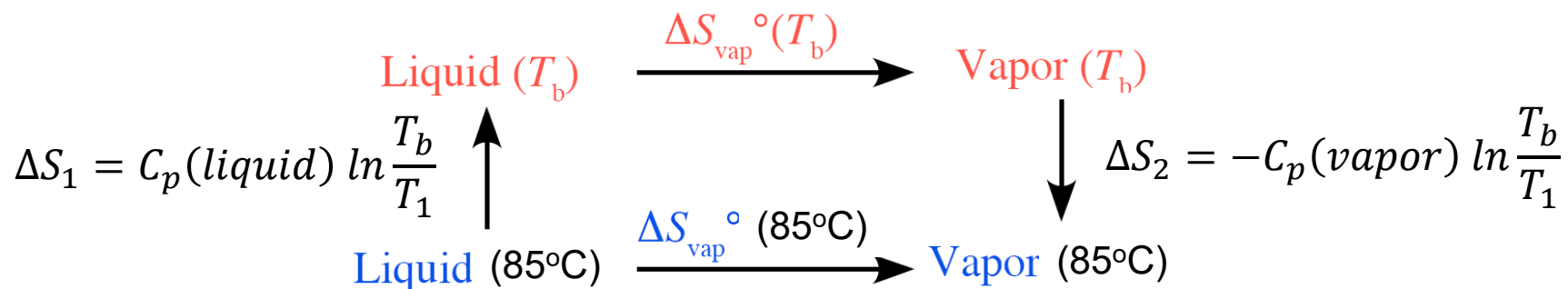
$$\Delta S_{\text{vap}}(25^\circ\text{C}) = \Delta S_1(\text{liquid heating; } 25^\circ\text{C} \rightarrow T_b) + \Delta S_{\text{vap}}(T_b) + \Delta S_2(\text{vapor cooling; } T_b \rightarrow 25^\circ\text{C})$$



8.43 Calculate the standard entropy of vaporization of water at 85 °C, given that its standard entropy of vaporization at 100 °C is 109.0 J·K⁻¹·mol⁻¹ and the molar heat capacities at constant pressure of liquid water and water vapor are 75.3 J·K⁻¹·mol⁻¹ and 33.6 J·K⁻¹·mol⁻¹, respectively, in this range.

For 1 mol of gas,

$$\Delta S_{\text{vap}}(85^\circ\text{C}) = \Delta S_1(\text{liquid heating; } 85^\circ\text{C} \rightarrow T_b) + \Delta S_{\text{vap}}(T_b) + \Delta S_2(\text{vapor cooling; } T_b \rightarrow 85^\circ\text{C})$$



Step 1, heating the reactants to 100 °C :

$$\Delta S_1 = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) = (75.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln\left(\frac{373 \text{ K}}{358 \text{ K}}\right) = 3.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Step 2, the entropy of vaporization of H₂O at 100 °C is 109.0 J · K⁻¹ · mol⁻¹

Step 3, cooling the products to 85 °C :

$$\Delta S_3 = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) = (33.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln\left(\frac{358 \text{ K}}{373 \text{ K}}\right) = -1.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Therefore, the molar entropy of vaporization is H₂O at 85 °C is:

$$\Delta S_{v,m} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 111 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

13.5 ENTROPY CHANGES AND SPONTANEITY

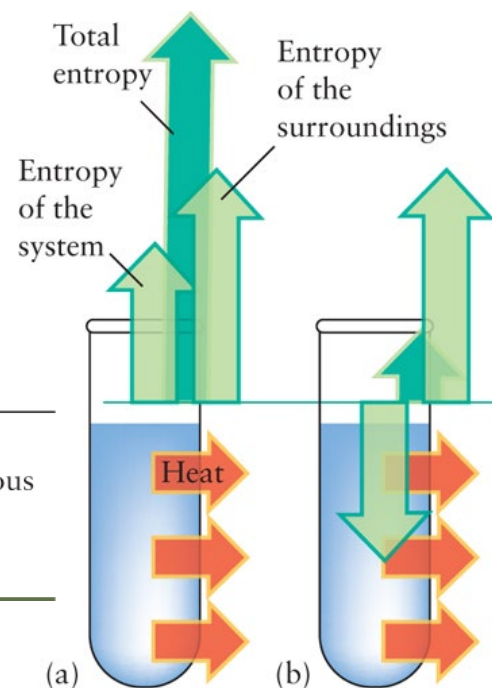
➤ Entropy change for surroundings

$$q_{\text{surr}} = -H_{\text{sys}} \quad (\text{const } P) \quad \rightarrow \quad \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}}$$

➤ ΔS_{tot} for the thermodynamic universe

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

ΔS	ΔS_{surr}	ΔS_{tot}	Character
>0	>0	>0	spontaneous
<0	<0	<0	not spontaneous; reverse change is spontaneous
>0	<0		spontaneous if ΔS is greater than $-\Delta S_{\text{surr}}$
<0	>0		spontaneous if ΔS_{surr} is greater than $-\Delta S$



EXAMPLE 13.6

Ice-water bath at 0°C, 1 atm with 20 g ice.

10.0 g of ice melts with a piece of Ni at 100°C. $\Delta S_{\text{tot}} = ?$

$$c_{s,P}(\text{Ni}) = 0.46 \text{ J K}^{-1} \text{ g}^{-1}, \quad c_{s,P}(\text{H}_2\text{O}) = 2.09 \text{ J K}^{-1} \text{ g}^{-1},$$

$$\Delta H_{\text{fus}}(\text{ice}) = 334 \text{ J g}^{-1}$$

System (Ni), Surroundings (ice-water bath at 0°C)

(1) Calculate the mass of Ni

heat lost by Ni = heat gained by ice-water bath
= heat used in melting ice

$$M_{\text{Ni}} c_{s,P}(\text{Ni}) \Delta T = M_{\text{Ice(melt)}} \Delta H_{\text{fus}}(\text{ice})$$

$$M_{\text{Ni}}(0.46)(373.15 - 273.15) = (10.0) (334) \rightarrow M_{\text{Ni}} = 73 \text{ g}$$

(2) Calculate ΔS_{sys} ($=\Delta S_{\text{Ni}}$)

$$\Delta S = nc_P \ln (T_2/T_1) = Mc_{s,P} \ln (T_2/T_1)$$

$$\Delta S_{\text{Ni}} = (73 \text{ g})(0.46 \text{ J K}^{-1} \text{ g}^{-1}) \ln (273.15/373.15) = -10 \text{ J K}^{-1}$$

(3) Calculate ΔS_{surr}

$$\begin{aligned} \Delta S_{\text{surr}} &= -\Delta H_{\text{sys}} / T_{\text{surr}} = -[-M_{\text{ice}}\Delta H_{\text{fus}}(\text{ice})] / T_{\text{bath}} \\ &= (10.0 \text{ g})(334 \text{ J g}^{-1})/273.15 \text{ K} = 12 \text{ J K}^{-1} \end{aligned}$$

(4) Calculate ΔS_{tot}

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -10 + 12 = +2 \text{ J K}^{-1}$$

$\Delta S_{\text{tot}} > 0 \rightarrow$ **spontaneous process !**

❖ Irreversible Expansion of an Ideal Gas

In an irreversible expansion, $P_{\text{ext}} < P$.

$$w_{\text{irrev}} = -P_{\text{ext}} dV > -PdV = w_{\text{rev}}$$

$$-w_{\text{irrev}} < -w_{\text{rev}}, \quad q_{\text{irrev}} < q_{\text{rev}} \quad (\Delta U = w_{\text{irrev}} + q_{\text{irrev}} = w_{\text{rev}} + q_{\text{rev}})$$

$$\rightarrow \Delta S = \frac{q_{\text{rev}}}{T} > \frac{q_{\text{irrev}}}{T}$$

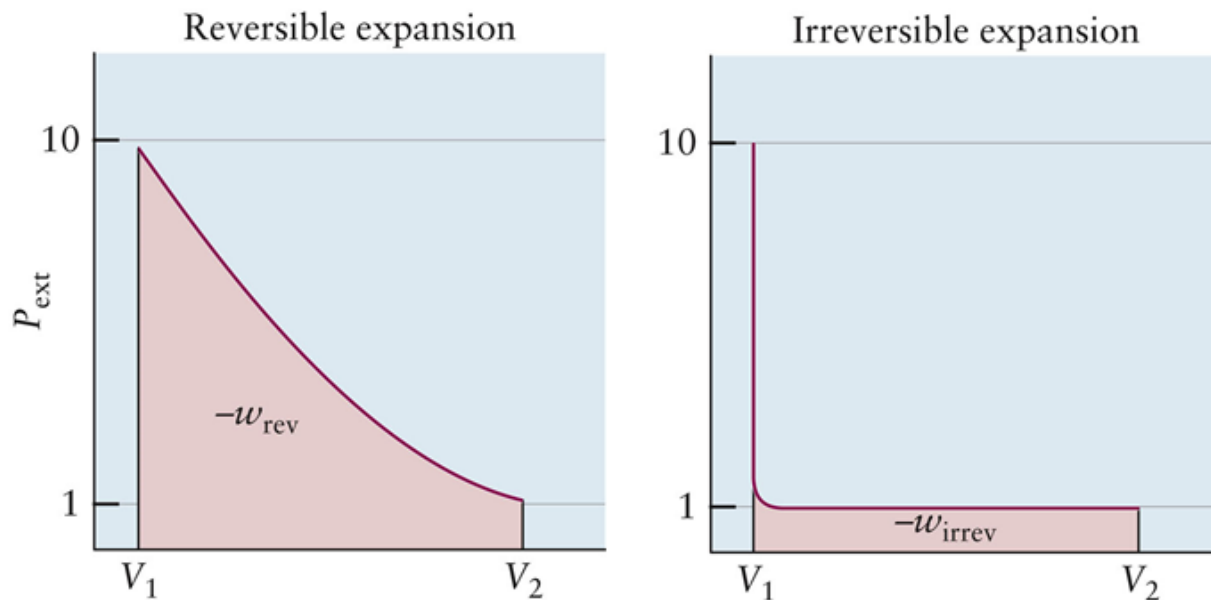


Fig. 13.5 Work done by a system in reversible and irreversible expansions.

➤ Clausius inequality

For the same pair of initial and final states, $q_{\text{rev}} > q_{\text{irrev}}$

$$\Delta S = \frac{q_{\text{rev}}}{T} > \frac{q_{\text{irrev}}}{T} \rightarrow \boxed{\Delta S \geq \frac{q}{T}} : \text{Clausius inequality}$$

For an *isolated* system, $q = 0 \rightarrow \Delta S > 0$

In a spontaneous process, the entropy of the universe increases.

❖ The Second Law of Thermodynamics

$$\begin{aligned} \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} &> 0 \text{ (Irreversible process, Spontaneous)} \\ &= 0 \text{ (Reversible process)} \end{aligned}$$

EXAMPLE 8.12 Calculate ΔS , ΔS_{surr} , and ΔS_{tot} for (a) the isothermal, reversible expansion and (b) the isothermal, free expansion of 1.00 mol of ideal gas molecules from 8.00 L to 20.00 L at 292 K. Explain any differences between the two path.

(a) Isothermal reversible expansion at 292 K

$$\Delta S = nR \ln \frac{V_2}{V_1} = 1.00 \times 8.3145 \times \ln \frac{20.00}{8.00} = +7.6 \text{ J/K}$$

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} \Rightarrow q_{\text{rev}} = -w_{\text{rev}} (\leftarrow \Delta U = 0) \Rightarrow q_{\text{surr}} = -q_{\text{rev}} = w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -nR \ln \frac{V_2}{V_1} = -7.6 \text{ J/K} = -\Delta S$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}} = 0; \text{ reversible}$$

(b) Isothermal free expansion 292 K

$$\Delta S = \Delta S_{\text{rev}} = nR \ln \frac{V_2}{V_1} = +7.6 \text{ J/K}; \text{ state function}$$

$$P_{\text{ext}} = 0 \Rightarrow w = 0 \Rightarrow q = -w = 0 \Rightarrow q_{\text{surr}} = -q = 0 \Rightarrow \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = 0$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}} = \Delta S = +7.6 \text{ J/K} > 0; \text{ irreversible}$$

→ useful to define absolute values of entropy relative to some reference state.

13.6 THE THIRD LAW OF THERMODYNAMICS

◆ *The Third Law of Thermodynamics*

- (a) $S \rightarrow 0$ as $T \rightarrow 0$ K for any pure substance in its equilibrium.
- (b) The absolute zero temperature can not be obtained by finite processes.

❖ **Absolute molar entropy S^0**
at 298.15 K and 1 atm

$$S^0 = \int_0^{298.15} \frac{C_P}{T} dT + \sum \Delta S_{\text{phase}}$$

$$\Delta S = S_f - S_i = \int_i^f \frac{dq_{\text{rev}}}{T}$$

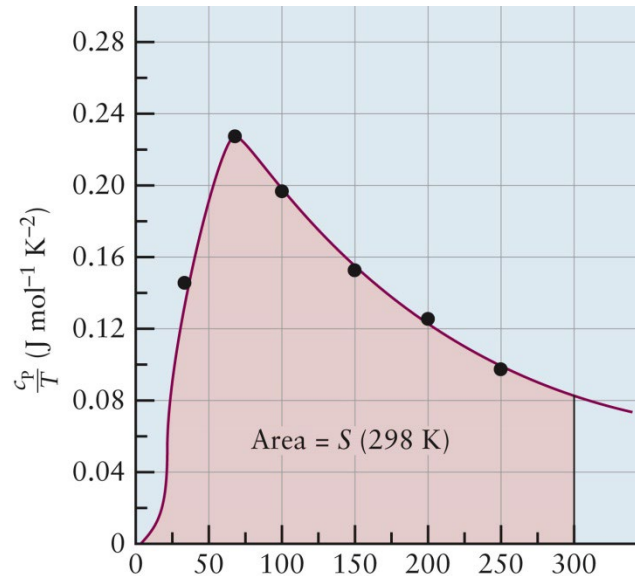
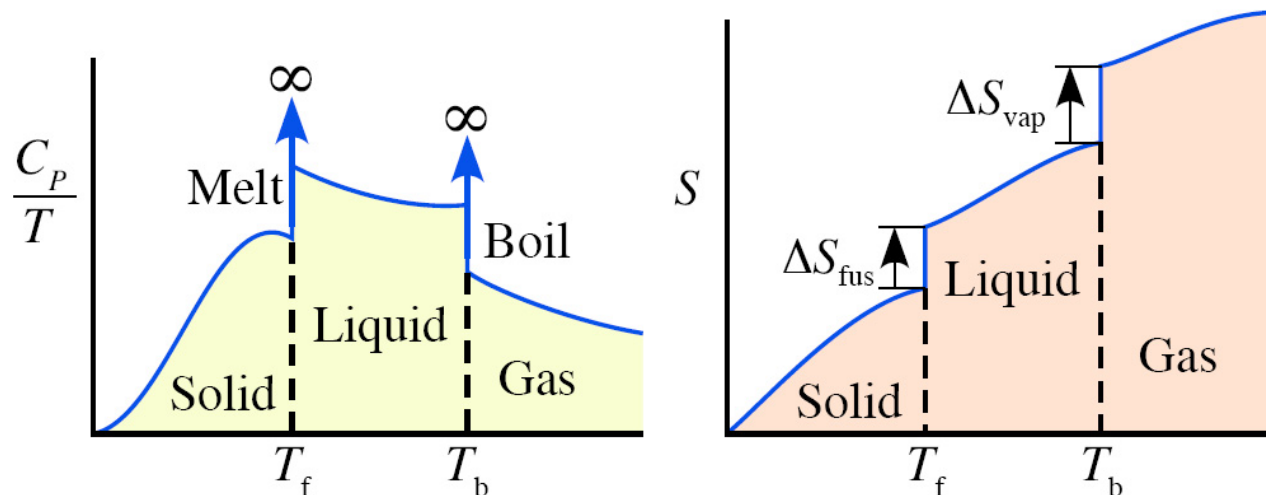


Fig. 13.6. A graph of c_p/T vs. T for Pt.



$$S_m^\circ = \int_0^{298.15} \frac{C_P}{T} dT + \sum \Delta S_{\text{phase}}$$



Gases	S_m°	Liquids	S_m°	Solids	S_m°
ammonia, NH ₃	192.4	benzene, C ₆ H ₆	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO ₂	213.7	ethanol, C ₂ H ₅ OH	160.7	calcium carbonate, CaCO ₃ [†]	92.9
hydrogen, H ₂	130.7	water, H ₂ O	69.9	diamond, C	2.4
nitrogen, N ₂	191.6			graphite, C	5.7
oxygen, O ₂	205.1			lead, Pb	64.8

*Additional values are given in Appendix 2A.

[†]Calcite.

at 25 °C

→ It would be much more convenient to have a state function that predicts the feasibility of a process in the system without explicit calculations for the surroundings.

13.7 THE GIBBS FREE ENERGY

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$S_{\text{tot}} = S_{\text{sys}} + S_{\text{surr}} = S_{\text{sys}} - H_{\text{sys}} / T = -(H_{\text{sys}} - TS_{\text{sys}}) / T$$

$$\Delta S_{\text{tot}} = -\frac{\Delta(H_{\text{sys}} - TS_{\text{sys}})}{T}$$

➤ Gibbs free energy: $G \equiv H - TS$ → $\Delta S_{\text{tot}} = \frac{-\Delta G_{\text{sys}}}{T}$

$\Delta S_{\text{tot}} > 0$ spontaneous (irrev)

$\Delta S_{\text{tot}} = 0$ reversible

$\Delta S_{\text{tot}} < 0$ impossible

At constant T and P ,

$\Delta G_{\text{sys}} < 0$ spontaneous

$\Delta G_{\text{sys}} = 0$ reversible

$\Delta G_{\text{sys}} > 0$ nonspontaneous

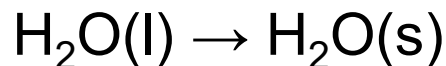
◆ Competition between ΔH and $T\Delta S$

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

In general,

$$\Delta H < 0 \text{ \& } \Delta S > 0 \rightarrow \Delta G < 0$$

In freezing,



$\Delta H < 0$ in favor of freezing

~ dominates when $T < T_f$

$\Delta S < 0$ in disfavoring freezing

~ dominates when $T > T_f$

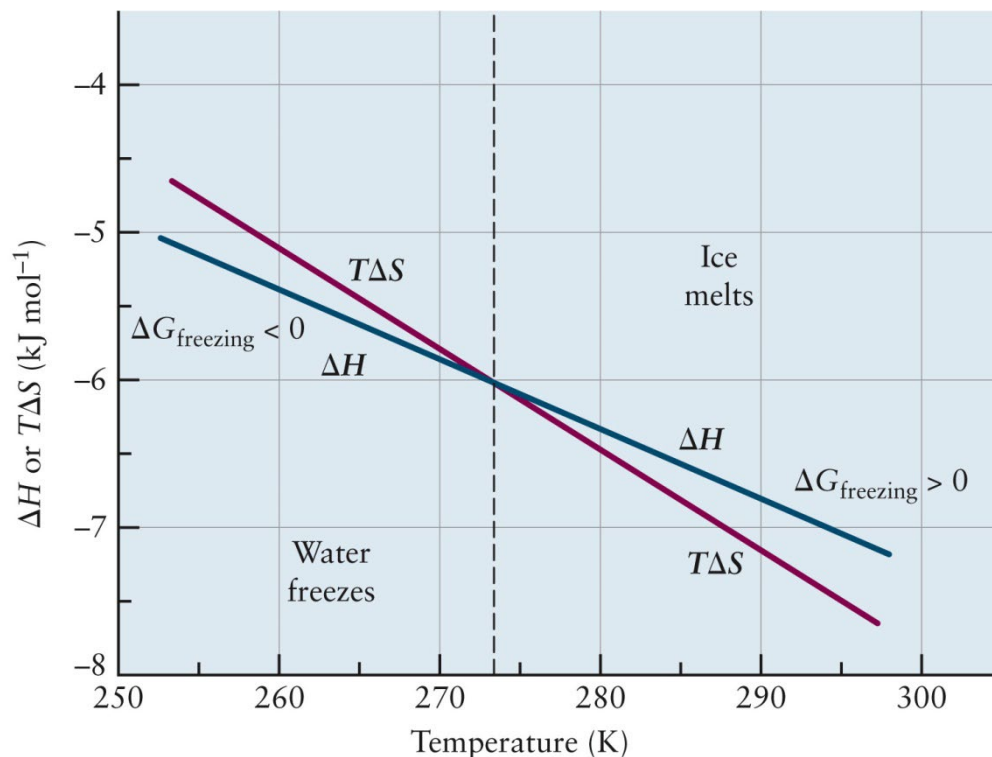


Fig. 13.8 Plots of ΔH and $T\Delta S$ vs. temperature for the freezing of water.

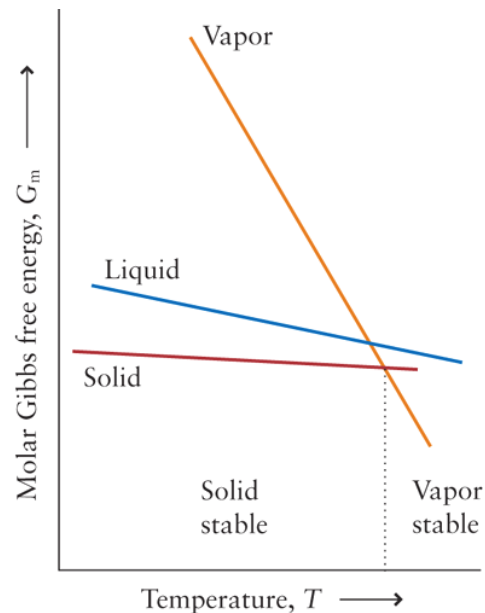
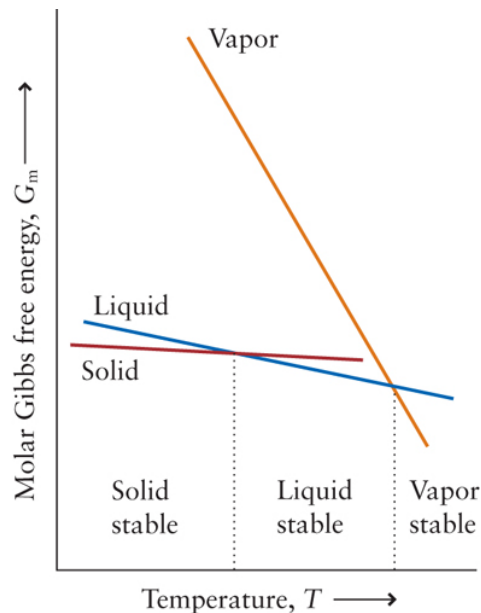
- G decreases as its T is raised at constant P .

$$\mathbf{G\downarrow = H - T\uparrow S} \quad ; \text{ H and S vary little with T, } S > 0$$

- Decreasing rate of G_m : vapor \gg liquid $>$ solid

$$S_m(\text{vapor}) \gg S_m(\text{liquid}) > S_m(\text{solid})$$

- Thermodynamic origin of phase transition



no stable
liquid phase
 CO_2

◆ Effects of Temperature on ΔG°

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(1) $\Delta H^\circ < 0$, $\Delta S^\circ > 0$

→ $\Delta G^\circ < 0$ at all T

(2) $\Delta H^\circ > 0$, $\Delta S^\circ < 0$

→ $\Delta G^\circ > 0$ at all T

(3) $\Delta G^\circ = 0$ at $T^* = \Delta H^\circ / \Delta S^\circ$

a) $\Delta H^\circ < 0$, $\Delta S^\circ < 0$

→ $\Delta G^\circ < 0$ at $T < T^*$

b) $\Delta H^\circ > 0$, $\Delta S^\circ > 0$

→ $\Delta G^\circ < 0$ at $T > T^*$

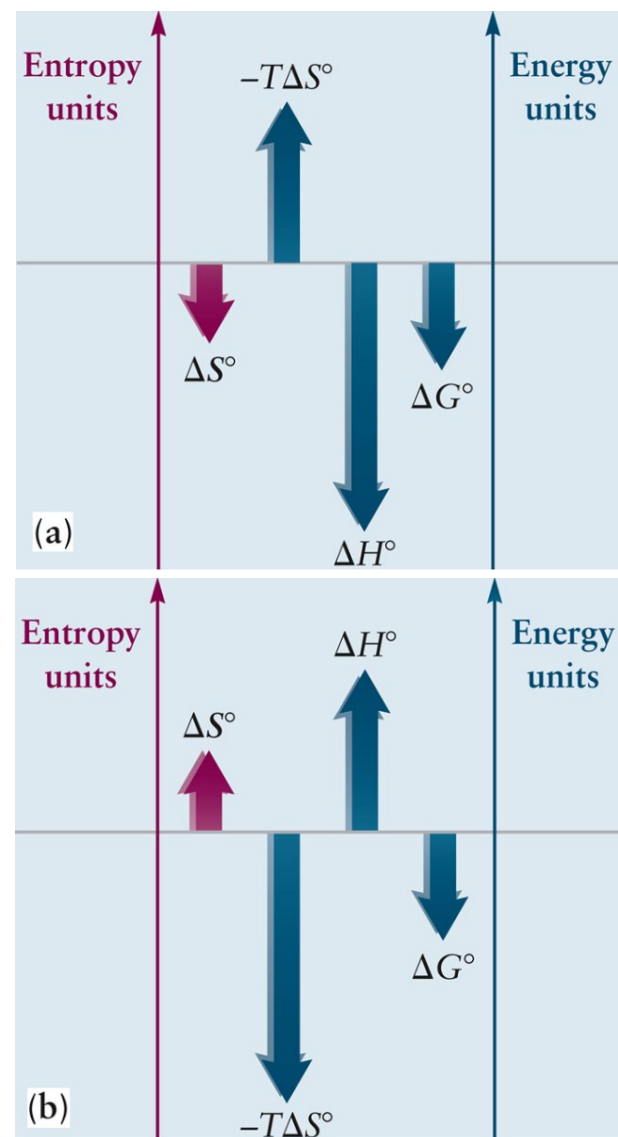


Fig. 13.11 Spontaneous processes from competition between ΔH° and ΔS° .

EXAMPLE 8.16

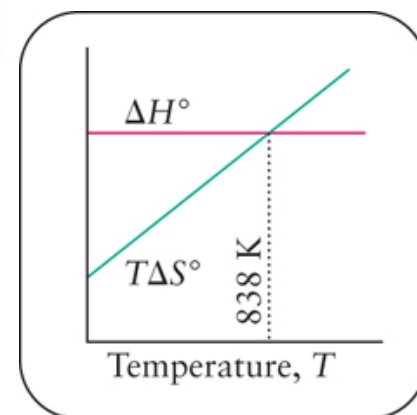
Estimate T at which it is thermodynamically possible for carbon to reduce iron(III) oxide to iron under standard conditions by the endothermic reaction. (using ΔH_f° and S_m°)



$$\begin{aligned} \Delta H^\circ &= (3 \text{ mol}) \times \Delta H_f^\circ(\text{CO}_2, \text{g}) - (2 \text{ mol}) \times \Delta H_f^\circ(\text{Fe}_2\text{O}_3, \text{s}) \\ &= 3(-393.5) - 2(-824.2) \text{ kJ} \\ &= +467.9 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= \{(4 \text{ mol}) \times S_m^\circ(\text{Fe}, \text{s}) + (3 \text{ mol}) \times S_m^\circ(\text{CO}_2, \text{g})\} \\ &\quad - \{(2 \text{ mol}) \times S_m^\circ(\text{Fe}_2\text{O}_3, \text{s}) + (3 \text{ mol}) \times S_m^\circ(\text{C}, \text{s})\} \\ &= \{4(27.3) + 3(213.7)\} - \{2(87.4) + 3(5.7)\} \text{ J}\cdot\text{K}^{-1} \\ &= +558.4 \text{ J}\cdot\text{K}^{-1} \end{aligned}$$

$$T = \frac{\overbrace{4.679 \times 10^5 \text{ J}}^{467.9 \text{ kJ}}}{558.4 \text{ J}\cdot\text{K}^{-1}} = 838 \text{ K, above } 565 \text{ }^\circ\text{C}$$



Summary for Reversible Processes in Ideal Gas

◆ Isochoric Process: $\Delta V = 0$

$$w = -P_{\text{ext}}\Delta V = 0 \quad q = q_v = nc_v\Delta T$$

$$\Delta U = q_v \quad \Delta H = \Delta U + \Delta(PV)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} dq_{\text{rev}} = \int_{T_1}^{T_2} \frac{nC_V}{T} dT = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

◆ Isobaric Process: $\Delta P = 0$

$$w = -P_{\text{ext}}\Delta V = -P\Delta V \quad q = q_p = nc_p\Delta T$$

$$\Delta U = w + q \quad \Delta H = q_p$$

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} dq_{\text{rev}} = \int_{T_1}^{T_2} \frac{nC_p}{T} dT = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

◆ Isothermal Process: $\Delta T = 0$

$$w = - \int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta U = (3/2)nR\Delta T = 0, \quad q = -w$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0$$

$$\Delta S = \frac{q}{T} = nR \ln \frac{V_2}{V_1}$$

◆ Adiabatic Process: $q = 0$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \Delta U = w = nc_v \Delta T \quad \Delta H = nc_p \Delta T$$

$$\Delta S = 0$$