

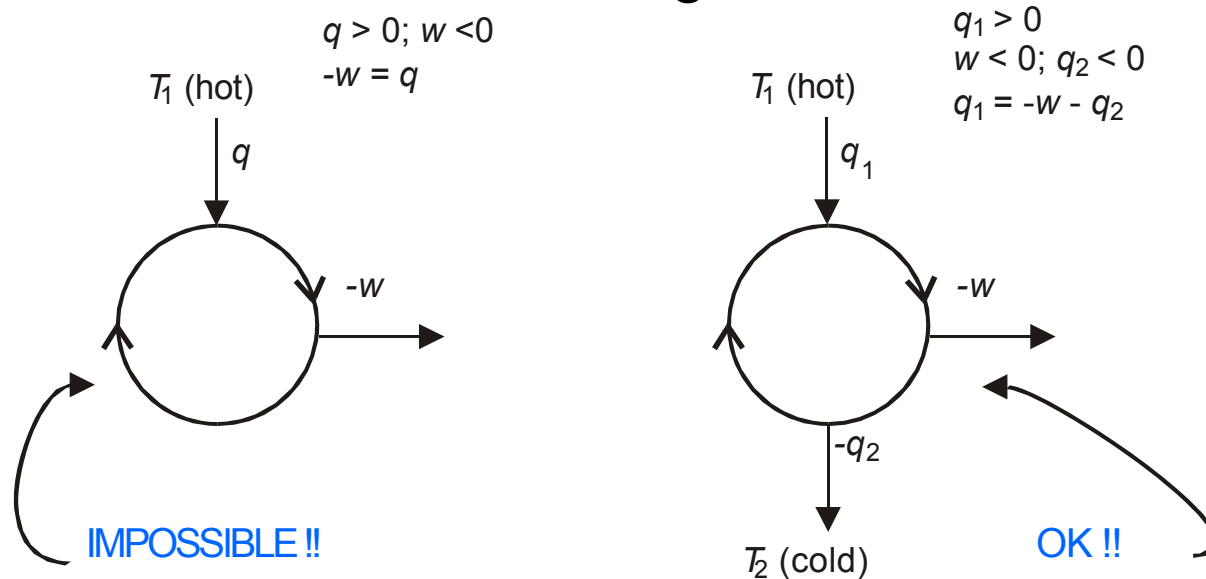
# Second Law of Thermodynamics

- Follows from observation of a directionality to natural or spontaneous processes
- Puts restrictions on useful conversion of  $q$  to  $w$
- Provides a set of principles for
  - determining the direction of spontaneous change
  - determining equilibrium state of system

# Second Law of Thermodynamics

## **Kelvin-Planck formulation**

It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings

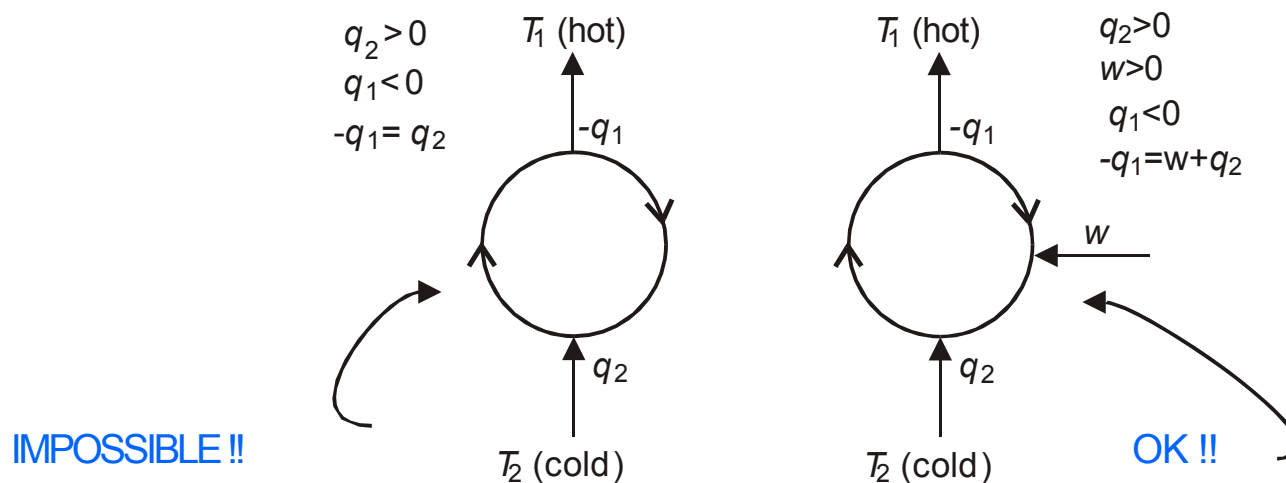


*Automobile engine operates in a cyclical process of fuel intake, compression, ignition and expansion, and exhaust.*

# Second Law of Thermodynamics

## Clausius formalism

Alternatively, but equivalent, statement: It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a cold reservoir and the flow of an equivalent amount of heat out of the system into a hot reservoir



# Second Law of Thermodynamics

## *Alternative Clausius statement*

All spontaneous processes are irreversible.

e.g. heat flows from hot to cold spontaneous and irreversibly

## *Mathematical statement*

$$\oint \frac{dq_{reversible}}{T} = 0 \quad \text{and} \quad \oint \frac{dq_{irreversible}}{T} \leq 0$$

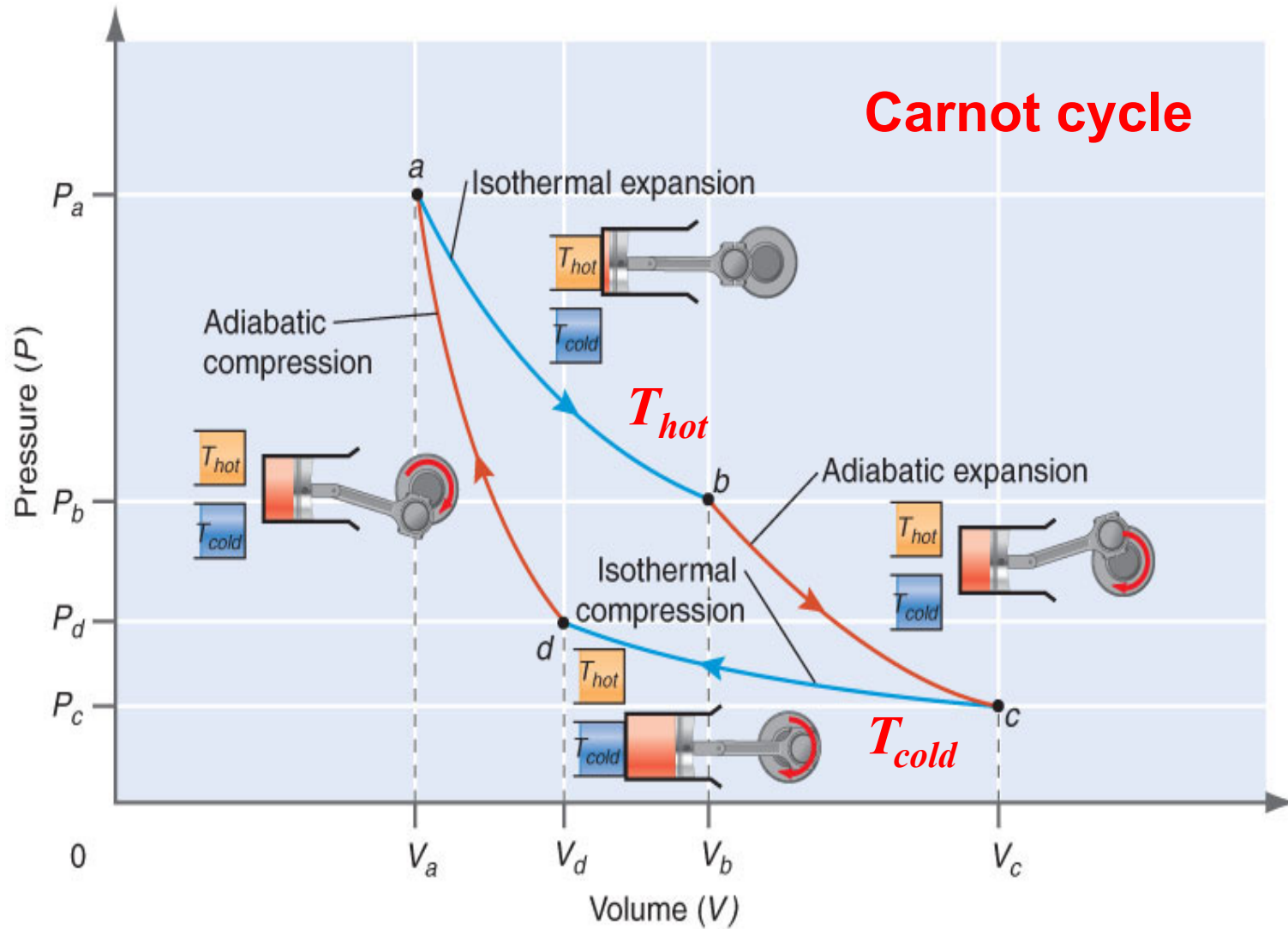
$$\int \frac{dq_{reversible}}{T} \text{ is a state function} = \int dS \quad \rightarrow \quad dS \equiv \frac{dq_{reversible}}{T}$$

**S = ENTROPY**

# Heat Engines and the Second Law

- Work can be converted to heat with 100% efficiency
- On the other hand, the conversion efficiency of heat to work is less than 100%, which limits the efficiency of heat engines. ***There is a natural asymmetry between converting work to heat and converting heat to work. Thermodynamics provides an explanation for this asymmetry.***
- The maximum work output in an isothermal expansion occurs in a reversible process. Thus the efficiency of the reversible heat engine is calculated (which provides an upper bound), even though a real engine operates irreversibly.

# Heat Engines and the Second Law



# Heat Engines and the Second Law

- To avoid losing heat to the surroundings at temperatures between  $T_{hot}$  and  $T_{cold}$ , the adiabatic segments 2 ( $b \rightarrow c$ ) and 4 ( $d \rightarrow a$ ) are used to move the gas between  $T_{hot}$  and  $T_{cold}$ .
- To absorb heat only at  $T_{hot}$  and release heat only at  $T_{cold}$ , segments 1 ( $a \rightarrow b$ ) and 3 ( $c \rightarrow d$ ) must be isothermal.

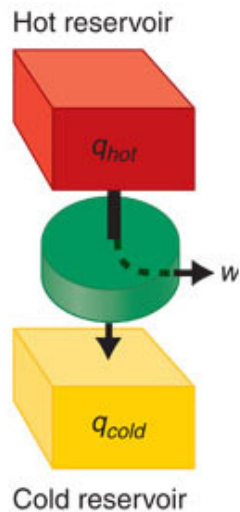
**TABLE 5.1**

## Heat, Work, and $\Delta U$ for the Reversible Carnot Cycle

Segment	Initial State	Final State	$q$	$w$	$\Delta U$
$a \rightarrow b$	$P_a, V_a, T_{hot}$	$P_b, V_b, T_{hot}$	$q_{ab} (+)$	$w_{ab} (-)$	$\Delta U_{ab} = 0$
$b \rightarrow c$	$P_b, V_b, T_{hot}$	$P_c, V_c, T_{cold}$	0	$w_{bc} (-)$	$\Delta U_{bc} = w_{bc} (-)$
$c \rightarrow d$	$P_c, V_c, T_{cold}$	$P_d, V_d, T_{cold}$	$q_{cd} (-)$	$w_{cd} (+)$	$\Delta U_{cd} = 0$
$d \rightarrow a$	$P_d, V_d, T_{cold}$	$P_a, V_a, T_{hot}$	0	$w_{da} (+)$	$\Delta U_{da} = w_{da} (+)$
Cycle	$P_a, V_a, T_{hot}$	$P_a, V_a, T_{hot}$	$q_{ab} + q_{cd} (+)$	$w_{ab} + w_{bc} + w_{cd} + w_{da} (-)$	$\Delta U_{cycle} = 0$

# Heat Engines and the Second Law

- From the Table in the previous slide it is seen that:  
 $W_{cycle} = W_{cd} + W_{da} + W_{ab} + W_{bc}$  and  $q_{cycle} = q_{ab} + q_{cd}$
- Because  $\Delta U_{cycle} = 0$ ,  $w_{cycle} = -(q_{cd} + q_{ab})$ ;  $q_{ab} > 0$  and  $q_{cd} < 0$
- By comparing the areas under the two expansion segments with those under the two compression segments in the indicator diagram one can see that the total work as seen from the system is negative, meaning that work is done on the surroundings in each cycle. **Since  $w_{cycle} < 0$ , so that  $|q_{ab}| > |q_{cd}|$**
- As shown in the figure below, not all of the heat withdrawn from the higher temperature reservoir is converted to work done by the system on the surroundings



- The efficiency,  $\varepsilon$ , of the reversible Carnot engine is defined as the ratio of the work output to the heat withdrawn from the hot reservoir:

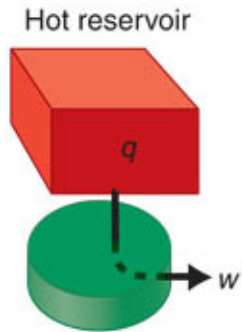
$$\varepsilon = \frac{q_{ab} + q_{cd}}{q_{ab}} = 1 - \frac{|q_{cd}|}{|q_{ab}|} < 1 \text{ because } |q_{ab}| > |q_{cd}|, q_{ab} > 0, \text{ and } q_{cd} < 0$$

- The above equation shows that the efficiency of a heat engine operating in a reversible Carnot cycle is always less than one.
- Equivalently, not all of the heat withdrawn from the hot reservoir can be converted to work.

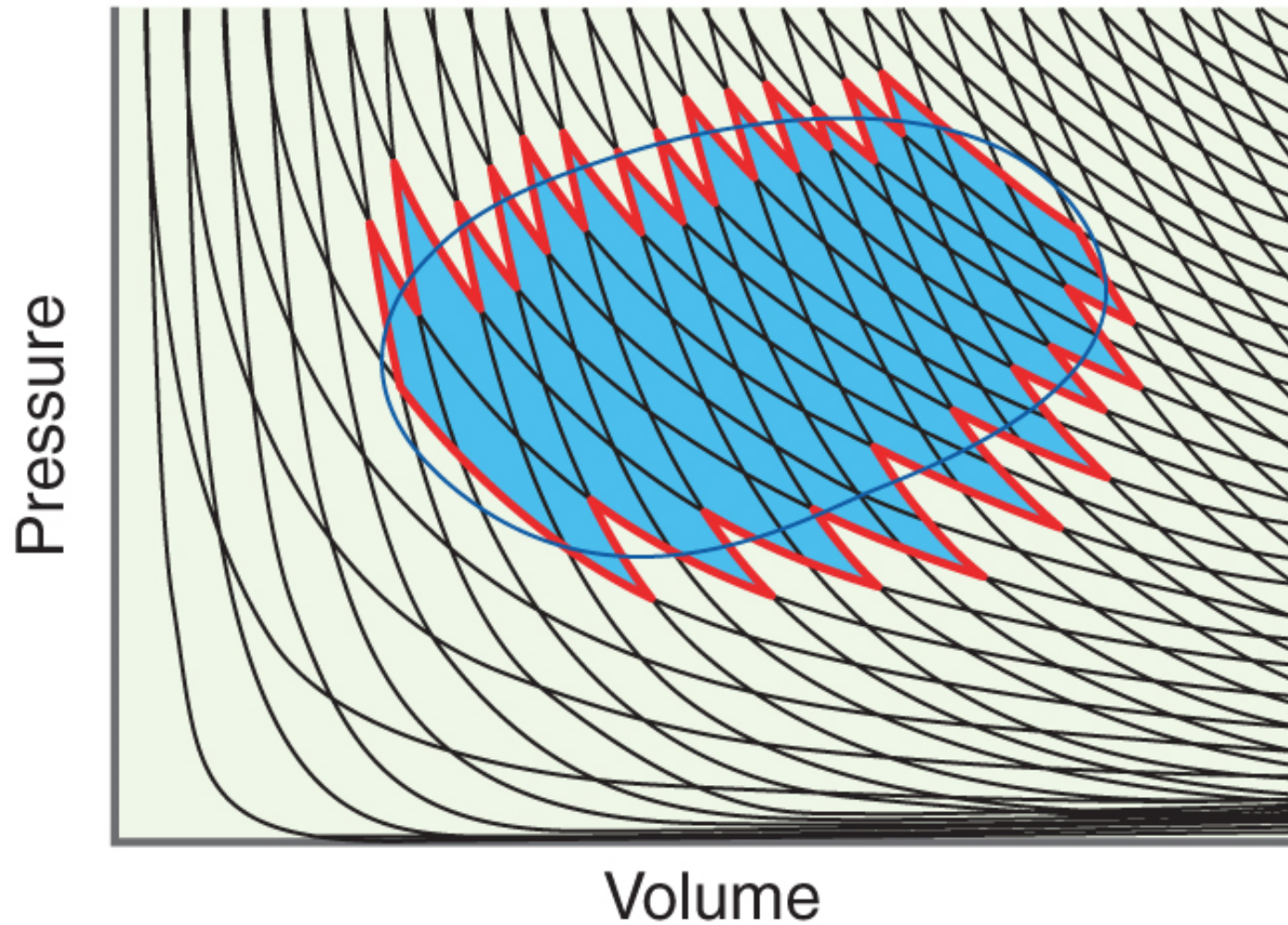


# Second Law of Thermodynamics

- The second law asserts that the heat engine depicted in figure cannot be constructed (if this were not valid then ***perpetual motion machines of the second kind could be constructed*** ).
- For an engine to produce work, the area of the cycle in a  $P$ - $V$  diagram must be greater than zero. However, this is impossible in a simple cycle using a single heat reservoir (if  $T_{hot} = T_{cold}$  in the Carnot cycle then the cycle collapses to a line, and the area of the cycle is zero).
- An arbitrary reversible cycle can be constructed that does not consist of individual adiabatic and isothermal segments. However, any reversible cycle can be approximated by a succession of adiabatic and isothermal segments, an approximation that becomes exact as the length of each segment approaches zero.



# Second Law of Thermodynamics



# Efficiency of a Reversible Heat Engine

- Reversible heat engine where the working substance in the engine is an **ideal gas**.

$$w_{ab} = -nRT_{hot} \ln \frac{V_b}{V_a} \quad w_{ab} < 0 \text{ because } V_b > V_a$$

$$w_{bc} = nC_{V,m} (T_{cold} - T_{hot}) \quad w_{bc} < 0 \text{ because } T_{cold} < T_{hot}$$

$$w_{cd} = -nRT_{cold} \ln \frac{V_d}{V_c} \quad w_{cd} > 0 \text{ because } V_d < V_c$$

$$w_{da} = nC_{V,m} (T_{hot} - T_{cold}) \quad w_{da} > 0 \text{ because } T_{hot} > T_{cold}$$

- The volume and temperature in the reversible adiabatic segments are related by:

$$T_{hot} V_b^{\gamma-1} = T_{cold} V_c^{\gamma-1} \quad \text{and} \quad T_{cold} V_d^{\gamma-1} = T_{hot} V_a^{\gamma-1}$$

- $V_c$  and  $V_d$  can be eliminated from the set of equations to yield:

$$w_{cycle} = -nR(T_{hot} - T_{cold}) \ln \frac{V_b}{V_a} < 0$$

- Because  $\Delta U_{a \rightarrow b} = 0$ , the heat withdrawn from the hot reservoir is

$$q_{ab} = -w = nRT_{hot} \ln \frac{V_b}{V_a}$$

- Thus, the efficiency of the reversible Carnot heat cycle with an ideal gas is

$$\varepsilon = \frac{|w_{cycle}|}{q_{ab}} = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}} < 1$$

- Heat can never be totally converted to work in a reversible cycle process. Since

$$W_{cycle, irreversible} < W_{cycle, reversible} \rightarrow \varepsilon_{irreversible} < \varepsilon_{reversible} < 1.$$

# Entropy

- Equating the two formulas for the efficiency of the reversible heat engine:

$$\frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{q_{ab} + q_{cd}}{q_{ab}} \text{ or } \frac{q_{ab}}{T_{hot}} + \frac{q_{cd}}{T_{cold}} = 0$$

- The last expression is the sum of the quantity  $q_{reversible}/T$  around the Carnot cycle. This result can be generalized to any reversible cycle made up of any number of segments to give the important result

$$\oint \frac{dq_{reversible}}{T} = 0$$

- The above equation can be regarded as the mathematical statement of the second law. Because the cyclic integral of  $dq_{reversible}/T$  is zero, this quantity must be the exact differential of a state function. This state function is called the **entropy**, and given the symbol  $S$ :

$$dS \equiv \frac{dq_{reversible}}{T}$$

- For a macroscopic change,
- $$\Delta S = \int \frac{dq_{reversible}}{T}$$

- Note that whereas  $dq_{reversible}$  is not an exact differential, multiplying this quantity by  $1/T$  makes the differential exact.

# Calculating Changes in Entropy

- It is important to note that  $\Delta S$  *must be calculated along a reversible path*. In considering an *irreversible process*,  $\Delta S$  must be calculated for an equivalent reversible process that proceeds between the same initial and final states corresponding to the irreversible process.
- Because  $S$  is a state function,  $\Delta S$  is necessarily path independent, *provided that the transformation is between the same initial and final states in both processes*.
- For any reversible adiabatic process,  $q_{reversible} = 0$ , so that  $\Delta S = 0$ . For any cyclic process,  $\Delta S = 0$ , because the change in any state function for a cyclic process is zero.
- For the reversible isothermal expansion or compression of an ideal gas, described by  $V_i, T_i \rightarrow V_f, T_i$ ,  $\Delta S$  can be calculated.

Because  $\Delta U = 0$  for this case,  $q_{reversible} = -w_{reversible} = nRT \ln \frac{V_f}{V_i}$

$$\Delta S = \int \frac{dq_{reversible}}{T} = \frac{1}{T} q_{reversible} = nR \ln \frac{V_f}{V_i}$$

- Note that  $\Delta S > 0$  for an expansion ( $V_f > V_i$ ) and  $\Delta S < 0$  for a compression ( $V_f < V_i$ ).

## Calculating Changes in Entropy...contd.

- Although the calculation is for a reversible process,  $\Delta S$  has exactly the same value for any reversible or irreversible isothermal path that goes between the same initial and final volumes and satisfies the condition that  $T_f = T_i$ . This is because  $S$  is a state function.

- Consider  $\Delta S$  for an ideal gas that undergoes a reversible change in  $T$  at constant  $V$  or  $P$ . For a reversible process described by  $V_i, T_i \rightarrow V_i, T_f$ ,  $dq_{reversible} = C_V dT$ , and

$$\Delta S = \int \frac{dq_{reversible}}{T} = \int \frac{nC_{V,m} dT}{T} \approx nC_{V,m} \ln \frac{T_f}{T_i}$$

- For a constant pressure process described by  $P_i, T_i \rightarrow P_i, T_f$ ,  $dq_{reversible} = C_P dT$

$$\Delta S = \int \frac{dq_{reversible}}{T} = \int \frac{nC_{P,m} dT}{T} \approx nC_{P,m} \ln \frac{T_f}{T_i}$$

- The last expressions in the above Equations are valid if the temperature interval is small enough that the temperature dependence of  $C_{V,m}$  and  $C_{P,m}$  can be neglected. Although  $\Delta S$  has been calculated for a reversible process, the above Equations hold for any reversible or irreversible process between the same initial and final states for any ideal gas.

## Calculating Changes in Entropy...contd.

- Since  $S$  is a state function,  $\Delta S$  is independent of path. Therefore, any reversible or irreversible process for an ideal gas described by  $V_i, T_i \rightarrow V_f, T_f$  can be treated as consisting of two segments (one constant volume and the other constant temperature), and similarly for  $P_i, T_i \rightarrow P_f, T_f$ . For the two step processes,  $\Delta S$  is given by (assuming that that temperature dependence of  $C_{V,m}$  and  $C_{P,m}$  can be neglected over the temperature range of interest)

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_{V,m} \ln \frac{T_f}{T_i} \quad \text{and} \quad \Delta S = -nR \ln \frac{P_f}{P_i} + nC_{P,m} \ln \frac{T_f}{T_i}$$

- Consider  $\Delta S$  for phase change. Experience shows that a liquid is converted to a gas at a constant boiling temperature through heat input if the process is carried out at constant pressure. Because  $q_P = \Delta H$ ,  $\Delta S$  for this reversible process is given by

$$\Delta S_{\text{vaporization}} = \int \frac{dq_{\text{reversible}}}{T} = \frac{q_{\text{reversible}}}{T_{\text{vaporization}}} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{vaporization}}}$$

- Similarly, for the phase change solid  $\rightarrow$  liquid,

$$\Delta S_{\text{fusion}} = \int \frac{dq_{\text{reversible}}}{T} = \frac{q_{\text{reversible}}}{T_{\text{fusion}}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

# Trouton's Rule

**Synoptic Table 3.1\*** Standard entropies (and temperatures) of phase transitions,  $\Delta_{\text{trs}}S^\ominus/(\text{J K}^{-1} \text{mol}^{-1})$

	Fusion (at $T_f$ )	Vaporization (at $T_b$ )
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, $\text{C}_6\text{H}_6$	38.00 (at 279 K)	87.19 (at 353 K)
Water, $\text{H}_2\text{O}$	22.00 (at 273.15 K)	109.0 (at 373.15 K)
Helium, He	4.8 (at 8 K and 30 bar)	19.9 (at 4.22K)

\* More values are given in the *Data section*.

**Synoptic Table 3.2\*** The standard entropies of vaporization of liquids

	$\Delta_{\text{vap}}H^\ominus/(\text{kJ mol}^{-1})$	$\theta_b/^\circ\text{C}$	$\Delta_{\text{vap}}S^\ominus/(\text{J K}^{-1} \text{mol}^{-1})$
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	-60.4	87.9
Methane	8.18	-161.5	73.2
Water	40.7	100.0	109.1

\* More values are given in the *Data section*.

- A wide range of liquids give approximately the same standard entropy of vaporization (about  $85 \text{ JK}^{-1} \text{ mol}^{-1}$ ): this empirical observation is called **Trouton's rule**
- Comparable changes in volume occurs (with an accompanying change in the number of accessible microstates) when any liquid evaporates and becomes a gas
- Liquids that show significant deviations from Trouton's rule do so on account of strong molecular interactions that restrict molecular motion – hydrogen bonding in water.



## Calculating Changes in Entropy...contd.

- Consider  $\Delta S$  for an arbitrary process involving real gases, solids, and liquids for which  $\beta$  and  $\kappa$ , but not the equation of state, are known (The detailed calculations are provided in Supplemental 5.12). For the system undergoing the change  $V_i, T_i \rightarrow V_f, T_f$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV = C_V \ln \frac{T_f}{T_i} + \frac{\beta}{\kappa} (V_f - V_i)$$

- For the system undergoing a change  $P_i, T_i \rightarrow P_f, T_f$  (Supplemental 5.13),

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

- For a solid or liquid, the last expression can be simplified if  $V$  and  $\beta$  are assumed constant over the  $T$  and  $P$  intervals of interest

$$\Delta S = C_P \ln \frac{T_f}{T_i} - V\beta(P_f - P_i)$$

- For ideal gas:  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T}$  and  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{P}$

# Calculating Changes in Entropy...contd.

## EXAMPLE PROBLEM 5.4

One mole of CO gas is transformed from an initial state characterized by  $T_i = 320.$  K and  $V_i = 80.0$  L to a final state characterized by  $T_f = 650.$  K and  $V_f = 120.0$  L. Using Equation (5.22), calculate for this process. Use the ideal gas values for  $\beta$  and  $\kappa$ . For CO,

$$C_{V,m} / \text{Jmol}^{-1} \text{K}^{-1} = 31.08 - 0.01452 T/\text{K} + 3.1415 \times 10^{-5} T^2/\text{K}^2 - 1.4973 \times 10^{-8} T^3/\text{K}^3$$

## EXAMPLE PROBLEM 5.5

2.50 mol of CO<sub>2</sub> gas is transformed from an initial state characterized by  $T_i = 450.$  K and  $P_i = 1.35$  bar to a final state characterized by  $T_f = 800.$  K and  $P_f = 3.45$  bar. Using Equation (5.23), calculate for this process. Assume ideal gas behavior and use the ideal gas value for  $\beta$ . For CO<sub>2</sub>,

$$C_{P,m} / \text{Jmol}^{-1} \text{K}^{-1} = 18.86 - 7.937 \times 10^{-2} T/\text{K} - 6.7834 \times 10^{-5} T^2/\text{K}^2 + 2.4426 \times 10^{-8} T^3/\text{K}^3$$

## EXAMPLE PROBLEM 5.6

3.00 mol of liquid mercury is transformed from an initial state characterized by  $T_i = 300.$  K and  $P_i = 1.00$  bar to a final state characterized by  $T_f = 600.$  K and  $P_f = 3.00$  bar. *a.* Calculate  $\Delta S$  for this process;  $\beta = 1.81 \times 10^{-4} \text{K}^{-1}$ ,  $\rho = 13.54 \text{g cm}^{-3}$ , and  $C_{P,m}$  for Hg (*l*) =  $27.98 \text{J mol}^{-1} \text{K}^{-1}$ . *b.* What is the ratio of the pressure-dependent term to the temperature-dependent term in  $\Delta S$ ? Explain your result.

# Entropy

- The thermodynamic function **entropy** allows one to predict the direction of spontaneous change for a system in a given initial state.
- Atoms and molecules have energetic degrees of freedom (*i.e.*, translational, rotational, vibrational, and electronic), each of which is associated with discrete energy levels that can be calculated using quantum mechanics. Quantum mechanics also characterizes a molecule by a state associated with a set of quantum numbers and a molecular energy.
- Entropy serves as a measure of the number of quantum states accessible to a macroscopic system at a given energy.
- Quantitatively,  $S = k \ln W$ , where  $W$  provides a measure of the number of states accessible to the system, and  $k = R/N_A$ .
- The **entropy of an isolated system is maximized at equilibrium**. Therefore, the approach to equilibrium can be envisioned as a process in which the system achieves the distribution of energy among molecules that corresponds to a maximum value of  $W$ , and correspondingly, to a maximum in  $S$ .
- Entropy measures the dispersal of energy, and the natural tendency of spontaneous change is toward states of higher entropy.

# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System

- *For an irreversible process in an isolated system, there is a unique direction of spontaneous change:*
  - $\Delta S > 0$  for the spontaneous process
  - $\Delta S < 0$  for the opposite or nonspontaneous direction of change
  - $\Delta S = 0$  only for a reversible process
- $\Delta S > 0$  is a criterion for a spontaneous change *only* if the system does not exchange energy in the form of heat and work with its surroundings.
- If any process occurs in the isolated system, it is by definition spontaneous and the entropy increases.
- *Whereas  $U$  can neither be created or destroyed,  $S$  for an isolated system can be created ( $\Delta S > 0$ ), but not destroyed.*

# The Change of Entropy in the Surroundings and

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings}$$

- The part of the surroundings that is relevant for entropy calculations is a thermal reservoir at a fixed temperature,  $T$ . The mass of the reservoir is sufficiently large that its temperature is only changed by an infinitesimal amount  $dT$  when heat is transferred between the system and surroundings.
- Consider the entropy change of the surroundings, whereby the surroundings are at either constant  $V$  or constant  $P$ . The amount of heat absorbed by the surroundings,  $dq_{surroundings}$ , depends on the process occurring in the system.
- If the surroundings are at constant  $V$ ,  $q_{surroundings} = \Delta U_{surroundings}$ , and if the surroundings are at constant  $P$ ,  $q_{surroundings} = \Delta H_{surroundings}$ .
- Because  $H$  and  $U$  are state functions, the amount of heat entering the surroundings is independent of the path.
- The system and surroundings need not be at the same temperature and  $q$  is the same whether the transfer occurs reversibly or irreversibly

# The Change of Entropy in the Surroundings and

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings}$$

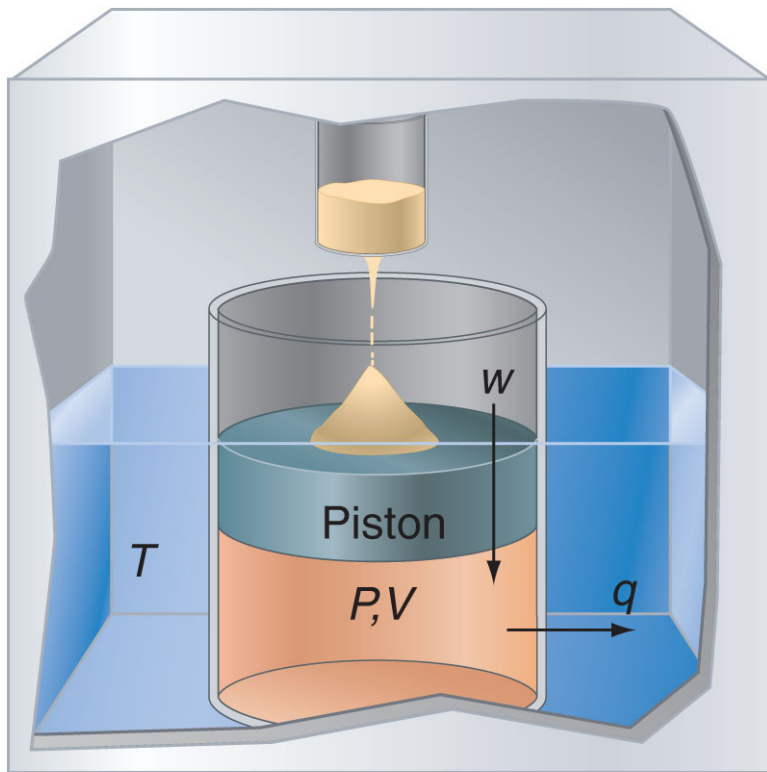
- Therefore,

$$dS_{surroundings} = \frac{dq_{surroundings}}{T_{surroundings}} \text{ or for a macroscopic change, } \Delta S_{surroundings} = \frac{q_{surroundings}}{T_{surroundings}}$$

- Note that the heat that appears in the above equation is the *actual* heat transferred. By contrast, in calculating  $\Delta S$  for the system using the heat flow,  $dq_{reversible}$  for a *reversible* process that connects the initial and final states of the system must be used, *not* the actual  $dq$  for the process.
- *It is essential to understand this reasoning in order to carry out calculations for  $\Delta S$  and  $\Delta S_{surroundings}$ .*

# The Change of Entropy in the Surroundings and

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings}$$



- Example Problem 5.7 and Example Problem 5.8. give examples for calculating the  $\Delta S$  and  $\Delta S_{surroundings}$  for reversible and irreversible isothermal compression processes
- For the reversible process,  $\Delta S = -\Delta S_{surroundings}$ , and  $\Delta S_{total} = 0$ . Because the process is reversible there is no direction of spontaneous change. For the irreversible process  $\Delta S$  is the same as the reversible process (as per definition). However,  $\Delta S_{surroundings}$  is different, so  $\Delta S_{total} \neq 0$
- *If the system and the part of the surroundings with which it interacts are viewed as an isolated composite system, the criterion for spontaneous change is  $\Delta S_{total} = \Delta S + \Delta S_{surroundings} > 0$ .*

## Second Law of Thermodynamics

(a) Irreversible: Consider the universe as an isolated system containing our initial system and its surroundings.

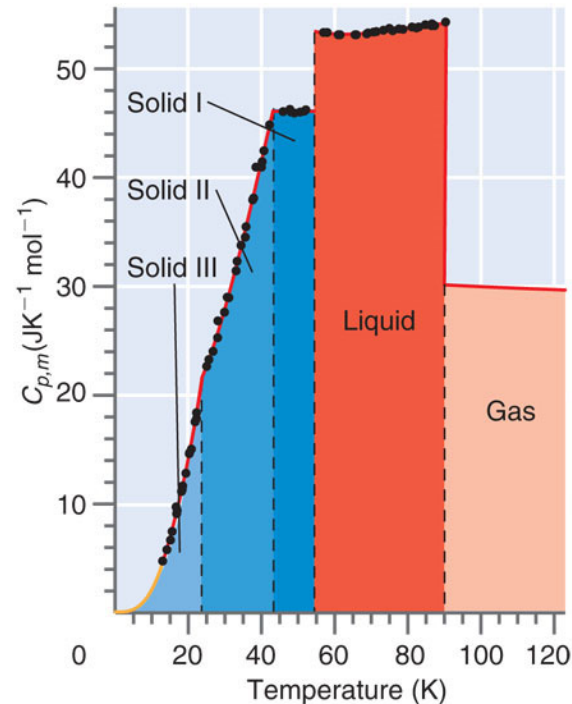
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$
$$\therefore \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$$

(b) Reversible:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S'_{\text{surroundings}} = 0$$
$$\therefore \Delta S'_{\text{surr}} = -\Delta S_{\text{sys}}$$



# Absolute Entropies and the Third Law of Thermodynamics



Experimental heat capacity of  $\text{O}_2$  as a function of temperature (1 bar pressure)

- $\text{O}_2$  has three solid phases, transition between them is observed at 23.66 K and 43.76 K
- The solid form melts to form a liquid at 54.39 K
- The liquid vaporizes to form a gas at 90.20 K
- Experimental data is available above 12.97 K; below this temperature, the data is extrapolated to zero Kelvin by assuming that  $C_{p,m} \propto T^3$ .

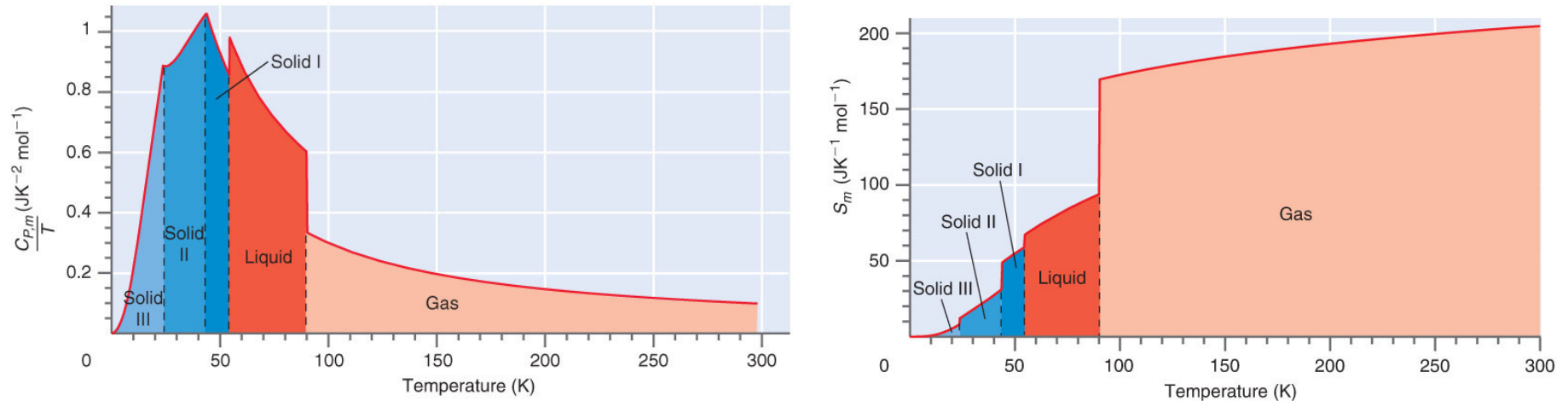
# Absolute Entropies and the Third Law of Thermodynamics

- Under constant pressure conditions, the molar entropy of the gas can be expressed in terms of the molar heat capacities of the solid, liquid, and gaseous forms and the enthalpies of fusion and vaporization as

$$S_m(T) = S_m(0 \text{ K}) + \int_0^{T_f} \frac{C_{P,m}^{\text{solid}} dT'}{T'} + \frac{\Delta H_{\text{fusion}}}{T_f} + \int_{T_f}^{T_b} \frac{C_{P,m}^{\text{liquid}} dT'}{T'} + \frac{\Delta H_{\text{vaporization}}}{T_b} + \int_{T_b}^T \frac{C_{P,m}^{\text{gas}} dT'}{T'}$$

- If the solid has more than one solid phase, each will give rise to a separate integral. To obtain a numerical value for  $S_m(T)$ , the heat capacity must be known down to zero kelvin, and  $S_m(0 \text{ K})$  must also be known.
- The **third law of thermodynamics** can be stated in the following form (due to Max Planck).
- The entropy of a pure, perfectly crystalline substance (element or compound) is zero at zero kelvin** (a perfectly crystalline solid has only one state at 0 K and  $S = k \ln W = k \ln 1 = 0$ ).

# Absolute Entropies and the Third Law of Thermodynamics



- The  $C_{P,m}$  data is graphed in the form of  $C_{P,m} / T$  as shown in the left figure
- The entropy as a function of temperature obtained by numerically integrating the area under the curve in the left figure and adding the entropy changes associated with phase changes at the transition temperatures.
- The results for  $\text{O}_2$  are shown in right figure

# Absolute Entropies and the Third Law of Thermodynamics

- Because  $C_p / T$  in a single phase region and  $\Delta S$  for melting and vaporization are always positive,  $S_m$  for a given substance is greatest for the gas-phase species. The molar entropies follow the order  $S_m^{gas} > S_m^{liquid} > S_m^{solid}$ .
- The molar entropy increases with the size of a molecule, because the number of degrees of freedom increases with the number of atoms
  - a non-linear gas-phase molecule has three translational, three rotational, and  $3n - 6$  vibrational degrees of freedom.
  - a linear molecule has three translational, two rotational, and  $3n - 5$  vibrational degrees of freedom.
  - for a molecule in a liquid, the three translational degrees of freedom are converted to local vibrational modes.
- A solid has only vibrational modes. It can be modeled as a three-dimensional array of coupled harmonic oscillators
  - the solid has a wide spectrum of vibrational frequencies, and solids with a large binding energy have higher frequencies than more weakly bound solids.
  - because modes with high frequencies are not activated at low temperatures, weakly bound solids have a larger molar entropy than strongly bound solids at low and moderate temperatures.
- The entropy of all substances is a monotonically increasing function of temperature.

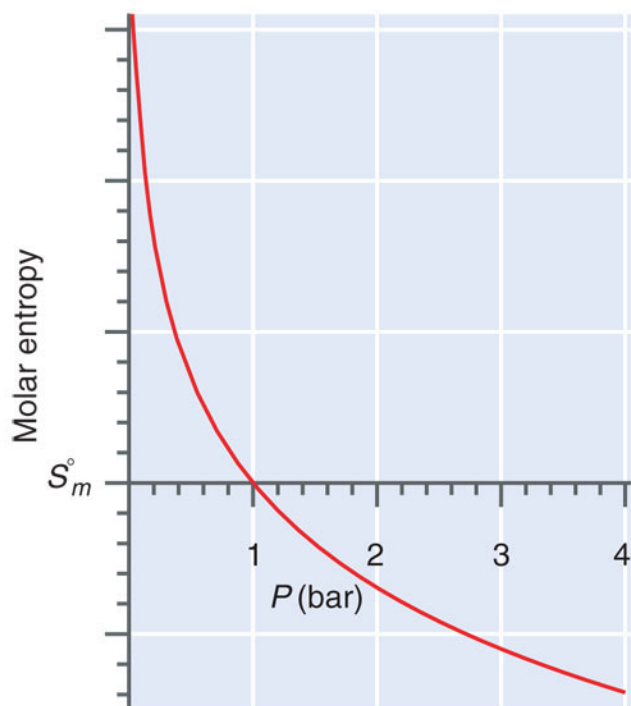
## Standard States in Entropy Calculations

- For  $S$ , the third law provides a natural definition of zero, namely, the crystalline state at zero Kelvin. Therefore, the absolute entropy of a compound can be experimentally determined from heat capacity measurements.
- Because  $S$  is a state function of pressure, tabulated values of entropies refer to a standard pressure of 1 bar. For an ideal gas at constant  $T$ ,

$$\Delta S_m = R \ln \frac{V_f}{V_i} = -R \ln \frac{P_f}{P_i}, \text{ Choosing } P_i = P^\circ = 1 \text{ bar,}$$

$$S_m(P) = S_m^\circ - R \ln \frac{P(\text{bar})}{P^\circ}$$

# Standard States in Entropy Calculations



- The Equation,

$$S_m(P) = S_m^\circ - R \ln \frac{P(\text{bar})}{P^\circ}$$

provides a way to calculate the entropy of a gas at any pressure.

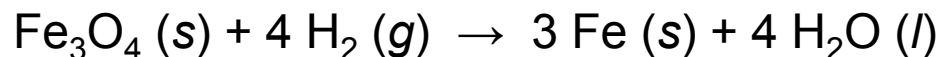
- For solids and liquids,  $S$  varies so slowly with  $P$  (as shown in section 5.4) that the pressure dependence of  $S$  can usually be neglected.

# Entropy Changes in Chemical Reactions

- Analogous to calculating  $\Delta H^{\circ}_R$  and  $\Delta U^{\circ}_R$  for chemical reactions,  $\Delta S^{\circ}_R$  is equal to the difference in the entropies of products and reactions, which can be written as

$$\Delta S^{\circ}_R = \sum_i \nu_i S^{\circ}_i$$

- For example, in the reaction



- The entropy change under standard state conditions of 1 bar and 298.15 K is given by

$$\begin{aligned}\Delta S^{\circ}_{298.15} &= 3S^{\circ}_{298.15} (\text{Fe}, \text{s}) + 4S^{\circ}_{298.15} (\text{H}_2\text{O}, \text{l}) - S^{\circ}_{298.15} (\text{Fe}_3\text{O}_4, \text{s}) - 4S^{\circ}_{298.15} (\text{H}_2, \text{g}) \\ &= 3 \times 27.28 \text{ JK}^{-1}\text{mol}^{-1} + 4 \times 69.61 \text{ JK}^{-1}\text{mol}^{-1} - 146.4 \text{ JK}^{-1}\text{mol}^{-1} - 4 \times 130.684 \text{ JK}^{-1}\text{mol}^{-1} \\ &= -308.9 \text{ JK}^{-1}\text{mol}^{-1}\end{aligned}$$

- For this reaction,  $\Delta S$  is large and negative primarily because gaseous species are consumed in the reaction.

## Entropy Changes in Chemical Reactions

- If  $\Delta n$  is the change in the number of moles of gas in the overall reaction, generally  $\Delta S^\circ$  is positive for  $\Delta n > 0$ , and negative for  $\Delta n < 0$ .
- Tabulated values of  $S^\circ$  are generally available at the standard temperature of 298.15 K, and values for selected elements and compounds are listed in Table 4.1 and 4.2 (Appendix B of the text).
- Calculate  $\Delta S^\circ$  at other temperatures. Calculations are carried out using the temperature dependence of  $S$ :

$$\Delta S_T^\circ = \Delta S_{298.15}^\circ + \int_{298.15}^T \frac{\Delta C_P^\circ}{T'} dT'$$

- The above equation is valid if no phase changes occur in the temperature interval between 298.15 K and  $T$ . If phase changes occur then associated entropy changes must be included

$$S_m(T) = S_m(0\text{ K}) + \int_0^{T_f} \frac{C_{P,m}^{\text{solid}}}{T'} dT' + \frac{\Delta H_{\text{fusion}}}{T_f} + \int_{T_f}^{T_b} \frac{C_{P,m}^{\text{liquid}}}{T'} dT' + \frac{\Delta H_{\text{vaporization}}}{T_b} + \int_{T_b}^T \frac{C_{P,m}^{\text{gas}}}{T'} dT'$$



## Questions on Concepts

**Q5.1)** Classify the following processes as spontaneous or not spontaneous and explain your answer. a) The reversible isothermal expansion of an ideal gas. b) The vaporization of superheated water at 102°C and 1 bar. c) The constant pressure melting of ice at its normal freezing point by the addition of an infinitesimal quantity of heat. d) The adiabatic expansion of a gas into a vacuum.

**Q5.2)** Why are  $\Delta S_{\text{fusion}}$  and  $\Delta S_{\text{vaporization}}$  always positive?

**Q5.3)** Why is the efficiency of a Carnot heat engine the upper bound to the efficiency of an internal combustion engine?

**Q5.4)** The amplitude of a pendulum consisting of a mass on a long wire is initially adjusted to have a very small value. The amplitude is found to decrease slowly with time. Is this process reversible? Would the process be reversible if the amplitude did not decrease with time?

**Q5.5)** A process involving an ideal gas is carried out in which the temperature changes at constant volume. For a fixed value  $\Delta T$ , the mass of the gas is doubled. The process is repeated with the same initial mass and  $\Delta T$  is doubled. For which of these processes is  $\Delta S$  greater? Why?

## Questions on Concepts

**Q5.6)** Under what conditions does the equality  $\Delta S = \frac{\Delta H}{T}$  hold?

**Q5.7)** Under what conditions is  $\Delta S < 0$  for a spontaneous process?

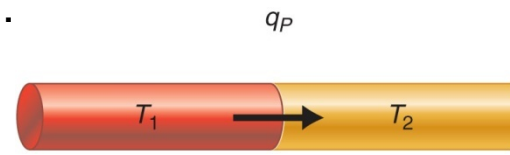
**Q5.8)** Is the equation valid  $\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV = C_V \ln \frac{T_f}{T_i} + \frac{\beta}{\kappa} (V_f - V_i)$  for an ideal gas?

**Q5.9)** Without using equations, explain why  $\Delta S$  for a liquid or solid is dominated by the temperature dependence of  $S$  as both  $P$  and  $T$  change.

**Q5.10)** You are told that  $\Delta S = 0$  for a process in which the system is coupled to its surroundings. Can you conclude that the process is reversible? Justify your answer.

# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System

- Consider the natural direction of change in a metal rod subject to a temperature gradient. Will the gradient become larger or smaller as the system approaches its equilibrium?
- Consider the **isolated** composite system shown in the Figure below. Two systems, in the form of metal rods with uniform, but different temperatures  $T_1 > T_2$  are brought into thermal contact (at constant pressure).



- Heat is withdrawn from the left rod; the same reasoning holds if the direction of heat flow is reversed.
- To calculate the  $\Delta S$  for this irreversible process using the heat flow, one must imagine a reversible process in which the initial and final states are the same as the irreversible process.
- The total change in temperature of the rod,  $\Delta T$  (assuming it is small enough that  $C_P$  is constant over the interval), is related to  $q_P$  by

$$dq_P = C_P dT \quad \text{or} \quad \Delta T = \frac{1}{C_P} \int dq_P = \frac{q_P}{C_P}$$

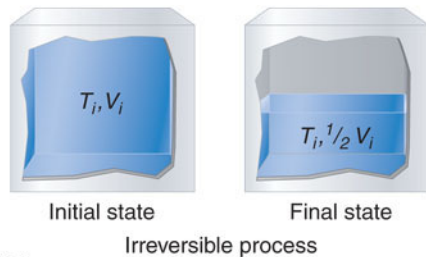
# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System...contd.

- Because the path is defined (constant pressure); it depends only on  $C_p$  and  $\Delta T$ . Moreover, because  $q_p = \Delta H$  and  $H$  is a state function,  $q_p$  is independent of the path between the initial and final states. Therefore,  $q_p = q_{reversible}$  if the temperature increment  $\Delta T$  is identical for the reversible and irreversible processes.
- Because the composite system is isolated,  $q_1 + q_2 = 0$  and  $q_1 = -q_2 = q_p$
- The entropy change of the composite system is the sum of the entropy change in each rod:
$$\Delta S = \frac{q_{reversible,1}}{T_1} + \frac{q_{reversible,2}}{T_2} = \frac{q_1}{T_1} + \frac{q_2}{T_2} = q_p \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$
- Because  $T_1 > T_2$ , the quantity in parenthesis is negative. This process has two possible directions:
  - if heat flows from the hotter to the colder rod, the temperature gradient will become smaller. In this case,  $q_p < 0$  and  $dS > 0$ .
  - if heat flows from the colder to the hotter rod, the temperature gradient will become larger. In this case,  $q_p > 0$  and  $dS < 0$ .

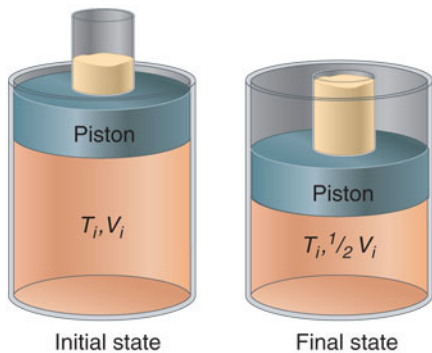
# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System...contd.

- Note that  $\Delta S$  has the same magnitude, but a different sign, for the two directions of change. Therefore,  $S$  appears to be a useful function for measuring the direction of natural change in an isolated system.
- Experience tells us that the temperature gradient will become less with time. *It can be concluded that the process in which  $S$  increases is the direction of natural change in an isolated system.*

# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System...contd.



(a)



(b)

- Consider the second process discussed previously in which an ideal gas spontaneously collapses to half its initial value without a force acting on it. This process and its reversible analog are shown in the left Figure (a and b). ( $w = 0$ )
- Because  $U$  does not change as  $V$  increases, and  $U$  is a function of  $T$  only for an ideal gas, the temperature remains constant in the irreversible process. ( $\Delta U = 0 \rightarrow q = 0$ )
- Therefore, the spontaneous irreversible process is both adiabatic and isothermal and is described by  $V_i, T_i \rightarrow \frac{1}{2} V_i, T_i$
- The imaginary reversible process with the same initial and final states as the irreversible process is shown in (b).
- In this process, the ideal gas undergoes a reversible isothermal transformation described by  $V_i, T_i \rightarrow \frac{1}{2} V_i, T_i$ . Because  $\Delta U = 0$ ,  $q = -w$ . The  $\Delta S$  for the process is:

$$\Delta S = \int \frac{dq_{reversible}}{T} = \frac{q_{reversible}}{T_i} = -\frac{w_{reversible}}{T_i} = nR \ln \frac{\frac{1}{2} V_i}{V_i} = -nR \ln 2 < 0$$

# Using Entropy to Calculate the Natural Direction of a Process in an Isolated System...contd.

- For the reverse process, in which the gas spontaneously expands so that it occupies twice the volume

$$\Delta S = nR \ln \frac{2V_i}{V_i} = nR \ln 2 > 0$$

- *Again, the process with  $\Delta S > 0$  is the direction of natural change in this isolated system. The reverse process ( $\Delta S < 0$ ) is the unnatural direction of change.*

# The Clausius Inequality

- The criterion to predict the natural direction of change in an isolated system ( $\Delta S > 0$ ) can also be obtained without considering a specific process.
- Consider the differential form of the first law for a process in which only  $P$ - $V$  work is possible:

$$dU = dq - P_{\text{external}} dV$$

- The above equation is valid for both reversible and irreversible processes. If the process is reversible, the above equation can be written in the following form:

$$dU = dq_{\text{reversible}} - PdV = TdS - PdV$$

- Because  $U$  is a state function,  $dU$  is independent of the path, and the above equation holds for both reversible and irreversible processes, as long as there are no phase transitions or chemical reactions, and only  $P$ - $V$  work occurs.
- To derive the Clausius inequality, we equate the above two expressions for  $dU$ :

$$dq_{\text{reversible}} - dq = (P - P_{\text{external}})dV$$

- If  $P - P_{\text{external}} > 0$ , the system will spontaneously expand, and  $dV > 0$ .  
If  $P - P_{\text{external}} < 0$ , the system will spontaneously contract, and  $dV < 0$ .  
In both cases,  $(P - P_{\text{external}})dV > 0$ .



# The Clausius Inequality

- Therefore, we can conclude that

$$dq_{\text{reversible}} - dq = TdS - dq \geq 0 \text{ or } TdS \geq dq$$

- The equality holds only for a reversible process. The **Clausius inequality** in the above equation for an irreversible process can be written in the form

$$dS > \frac{dq}{T}$$

- For an irreversible process in an isolated system,  $dq = 0$ . **Therefore, for any irreversible process in an isolated system,  $\Delta S > 0$ .**
- How can the results that  $dU = dq - P_{\text{external}}dV = TdS - PdV$  be reconciled with the fact that work and heat are path functions?
  - the answer is that  $dw \geq -PdV$  and  $dq \leq TdS$ , where the equality holds only for a reversible process. ( $(P - P_{\text{external}})dV > 0$  and  $dS > dq/T$ )
  - the results  $dq + dw = TdS - PdV$  states that the amount by which the work is greater than  $-PdV$  and the amount by which the heat is less than  $TdS$  in an irreversible process involving only  $PV$  work are exactly equal.
  - **therefore, the differential expression  $dU = TdS - PdV$  is obeyed for both reversible and irreversible processes.**

# The Clausius Inequality

- The Clausius inequality can be used to evaluate the cyclic integral  $\oint dq/T$  for an arbitrary process.
- Because  $dS = dq_{reversible}/T$ , the value of the cyclic integral is zero for a reversible process.

- Consider a process in which the transformation from state 1 to state 2 is reversible, but the transition from state 2 back to state 1 is irreversible:

$$\oint \frac{dq}{T} = \int_1^2 \frac{dq_{reversible}}{T} + \int_2^1 \frac{dq_{irreversible}}{T} = - \int_2^1 \frac{dq_{reversible}}{T} + \int_2^1 \frac{dq_{irreversible}}{T}$$

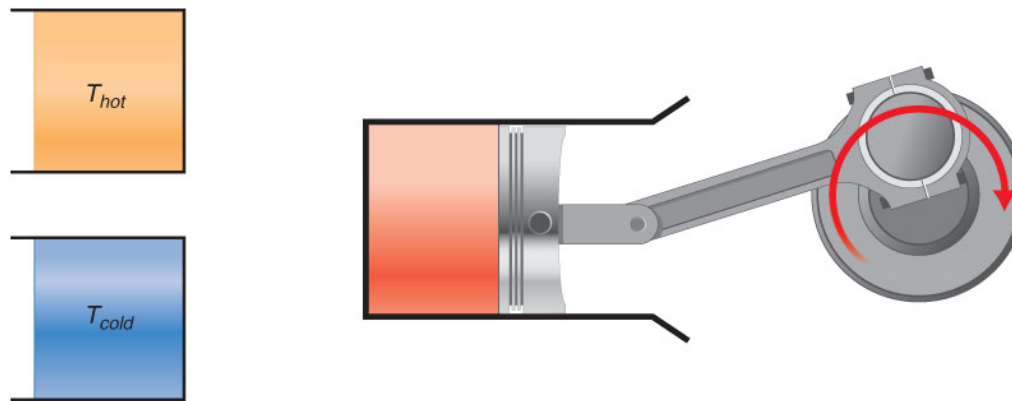
- Exchanging the limits as done in the above is only valid for a state function
- Because  $dq_{reversible} > dq_{irreversible}$  (Previous slide),

$$\oint \frac{dq}{T} \leq 0$$

- The equality holds only holds for a reversible process. Note that the cyclic integral of an exact differential is always zero, but the integrand in the Equation above is only an exact differential for a reversible process.

# Heat Engines and the Second Law

- An automobile engine operates in a cyclical process of fuel intake, compression, ignition and expansion, and exhaust
- This occurs several thousand times per minute and is used to perform work on the surroundings
- Because the work produced by such engines is a result of the heat released in a combustion process, they are referred to as **heat engines**



- The expansion and contraction of the gas caused by changes in its temperature drives the piston in and out of the cylinder. This linear motion is converted to circular motion using an eccentric, and the rotary motion is used to do work in the surroundings