

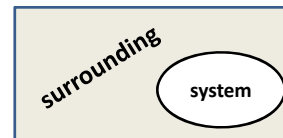
Thermodynamic definition of entropy

Change in **entropy** that occurs during a chemical or physical process

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev}}}{T}$$

For surroundings,

$$dS_{\text{surr}} = -dq/T_{\text{surr}}$$

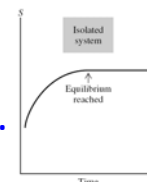


$$\Delta S_{\text{surr}} = \frac{-q}{T_{\text{surr}}}$$

Large change in entropy occurs when heat is dissipated to surrounding at low temperature.

Entropy and Equilibrium

For an isolated system, spontaneous changes will occur until the entropy is maximized. This leads to **equilibrium**.



For a closed system (heat and work exchange with surrounding is allowed), spontaneous changes will occur until the entropy of system plus surrounding, is maximized. This leads to equilibrium.

$$dS_{\text{total}} = dS_{\text{sys}} + dS_{\text{surr}} > 0 \quad \text{Spontaneous process}$$

$$dS_{\text{total}} = dS_{\text{sys}} + dS_{\text{surr}} = 0 \quad \text{Equilibrium process}$$

$$dS_{\text{total}} = dS_{\text{sys}} + dS_{\text{surr}} < 0 \quad \text{Impossible process}$$

For any process

$$dS_{\text{sys}} + dS_{\text{surr}} \geq 0$$

"=" for reversible, equilibrium

">" spontaneous (irreversible) (real)

Entropy and Reversibility

- Reversible process:

Reversible heat transfer between system and surrounding must occur with no finite temperature difference.

$$T_{\text{syst}} = T_{\text{surr}} \Rightarrow dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} = \frac{dq_{\text{rev}}}{T_{\text{syst}}} - \frac{dq}{T_{\text{surr}}} = 0$$

- Irreversible process (spontaneous):

The system + surrounding = universe, can be considered an isolated system.

For any isolated system, $dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} > 0$

$$\Delta S_{\text{univ}} > 0$$

Calculation of Entropy Changes (A few special cases)

1. Cyclic Process $\Delta S_{\text{syst}} = 0$ (S is a state function)

2. Reversible adiabatic process $\Delta S_{\text{syst}} = 0$ ($dq_{\text{rev}} = 0$)

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev}}}{T}$$

3. Reversible phase-change at constant p and T

$$\Delta S_{\text{syst}} = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T}$$

4. Constant p heating (reversibly) with no phase change:

$$dq_{\text{rev}} = dq_p = C_p dT \quad \Delta S_{\text{syst}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln \left(\frac{T_2}{T_1} \right)$$

5. Reversible isothermal process:

$$\Delta S_{\text{syst}} = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

6. For ideal gas:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{dU - w_{\text{rev}}}{T} = \frac{C_V dT + p dV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \Delta S = C_p \ln \frac{T_2}{T_1} + nR \ln \frac{p_1}{p_2}$$

Entropy change

The change in entropy of the system dS is defined in terms of reversible heat as dq_{rev}/T

$$dS = \frac{dq_{rev}}{T} > \frac{dq_{irrev}}{T}$$

If the system is reversible and adiabatic

$$dS = 0 > \frac{dq_{irrev}}{T}$$

$$dq_{irrev} < 0$$

If two states can be connected by a reversible adiabatic process, then any **irreversible process** connecting the two states **must** involve the removal of heat from the system

Example 1: Entropy changes for Phase Transitions

Phase transitions including fusion (i.e. melting), freezing, vaporization, condensation, etc. may be treated as reversible heat transfers occurring at constant temperature and pressure. Therefore...

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T} \int_i^f dq_{rev} = \frac{\Delta H}{T}$$

- Calculate the entropy change when 2 moles of liquid water vaporize at $T=373\text{K}$. Assume for $\Delta H_{vap} = 40,66\text{kJ} / \text{mole water}$

$$\Delta S = \frac{\Delta H_{vap}}{T} = (2 \text{ moles}) \frac{40,660 \text{ J} / \text{mole}}{373 \text{ K}} = 218.0 \text{ J} / \text{K}$$

Example 2: Entropy Change for a Reversible, Isothermal Expansion/Compression

- For an ideal gas, an isothermal expansion (i.e. $\Delta T=0$) means
 $\Delta E = n\bar{c}_V \Delta T = q_{rev} + w_{rev} = 0 \Rightarrow q_{rev} = -w_{rev}$
- $q_{rev} = -w_{rev} = \int_{V_1}^{V_2} P dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\left(\frac{V_2}{V_1}\right)$
- $\Delta S = \frac{q_{rev}}{T} = nR \ln\left(\frac{V_2}{V_1}\right)$

Calculate the entropy change when 5 moles of an ideal gas expand isothermally and reversibly from a volume of 10L to a volume of 50L.

Solution:

$$\Delta S = \frac{q_{rev}}{T} = nR \ln\left(\frac{V_2}{V_1}\right) = (5 \text{ moles})(8.31 \text{ J / mole} \cdot \text{K}) \ln\left(\frac{50 \text{ L}}{10 \text{ L}}\right) = (41.55 \text{ J / K}) \ln(5) = 66.87 \text{ J / K}$$

- Constant Pressure: $dq_p = dH = n\bar{c}_p dT$
 $\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{n\bar{c}_p dT}{T} = n\bar{c}_p \int_{T_1}^{T_2} \frac{dT}{T} = n\bar{c}_p \ln\left(\frac{T_2}{T_1}\right)$
- Constant Volume: $dq_v = dE = n\bar{c}_v dT$
 $\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{n\bar{c}_v dT}{T} = n\bar{c}_v \int_{T_1}^{T_2} \frac{dT}{T} = n\bar{c}_v \ln\left(\frac{T_2}{T_1}\right)$

Calculate the entropy change when 18 grams of water are heated from 300K to 350K at constant pressure. Assume $\bar{C}_p = 75.30 \text{ J / mole} \cdot \text{K}$.

$$\begin{aligned} \Delta S &= n\bar{c}_p \ln\left(\frac{T_2}{T_1}\right) = (18 \text{ g}) \left(\frac{1 \text{ mole}}{18 \text{ g}}\right) (75.30 \text{ J / mole} \cdot \text{K}) \ln\left(\frac{350 \text{ K}}{300 \text{ K}}\right) \\ &= (75.30 \text{ J / K}) \ln(1.17) = 11.82 \text{ J / K} \end{aligned}$$

An insulated water bath maintained at 273K contains 20 grams of ice. The pressure is constant at 1 atm. A piece of nickel at a temperature of 373K is dropped into the bath. The temperature of the bath does not change, but when the nickel cools to 273K, 10 grams of ice have melted. Calculate how much the nickel weighed, the entropy change of the nickel, the entropy change of the bath+ice (i.e. surroundings) and the entropy change of the universe. For nickel $\bar{C}_p = 0.46 J / g \cdot K$, for ice $\bar{C}_p = 2.09 J / g \cdot K$, and for ice $\Delta H_{fusion} = 334 J / g \cdot K$.

Solution:

- Calculate the weight of the nickel. This is done by using the First Law and saying the amount of heat that left the nickel equals the heat that was used to melt 10g of ice.

$$\text{Heat that left the nickel} = \Delta H = M\bar{C}_p\Delta T = -M(0.46 J / g \cdot K)(273K - 373K)$$

$$\text{Heat that melted 10g of ice} = (10g)\Delta H_{fusion} = (10g)(334 J / g) = 3340 J$$

$$\text{Equating these two heats: } -M(0.46 J / g \cdot K)(273K - 373K) = 3340 J \Rightarrow M = 73g$$

- Now calculate the entropy change in lowering the temperature of 73g of nickel from 373K to 273K at constant pressure.

$$\Delta S_{Ni} = M\bar{C}_p \ln\left(\frac{T_2}{T_1}\right) = (73g)(0.46 J / g \cdot K) \ln\left(\frac{273}{373}\right) = -10 J / K$$

- Now calculate the entropy change of the surroundings=ice+bath. This is the entropy change for melting 10g of ice

$$\Delta S_{bath+ice} = (10g) \frac{\Delta H_{fusion}}{T_{fusion}} = (10g) \frac{334 J / g \cdot K}{273K} = +12 J / K$$

The entropy change for the universe is the sum of the entropy change for the nickel (i.e. the system) and the entropy change for the bath+ice (i.e. the surroundings)

$$\Delta S_{universe} = \Delta S_{Ni} + \Delta S_{bath+ice} = (-10 + 12) J / K = 2 J / K$$

Comments: Note the entropy change for the system can be negative. The Second Law is not violated if the sum of the entropy changes of the system and surroundings is positive or zero.

Standard Molar Entropies

- According to the **Third Law of Thermodynamics**, the entropy of a pure, perfect crystal can be taken to be zero at 0 K.
- The **standard molar entropy, S°** , is the entropy of one mole of a substance in its standard state.
- Since entropy increases with temperature, standard molar entropies are positive—even for elements.

$$\Delta S = \sum v_p S^\circ(\text{products}) - \sum v_r S^\circ(\text{reactants})$$

The Third Law

- For substances in internal equilibrium, undergoing an isothermal process, the entropy change goes to zero as T (in K) goes to zero.

$$\lim_{T \rightarrow 0} \Delta S = 0$$

- The law is valid for pure substances and mixtures.
- Close to Zero Kelvin, the molecular motions have to be treated using quantum mechanics → still it is found that quantum ideal gases obey the third law.

Phenomenological description of the third law.

- There does not exist any finite sequence of cyclical processes, which can cool a body to zero Kelvin (absolute zero).

Calculation of Entropy at *any* temperature

Heating at constant pressure/Volume

$$\Delta S_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1}$$

$$\Delta S_V = \int \frac{C_V}{T} dT = C_V \ln \frac{T_2}{T_1}$$

Entropy at any temperature,

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} + \int_{T_b}^T \frac{C_p(g)}{T} dT$$

Debye Extrapolation: At low T , $C_p \propto T^3$

Trouton's Rule

A wide range of liquid give approx. the same standard entropy of vaporization $\sim 85 \text{ J K}^{-1} \text{ mol}^{-1}$. Exception: water, it is 109 J/K/mol

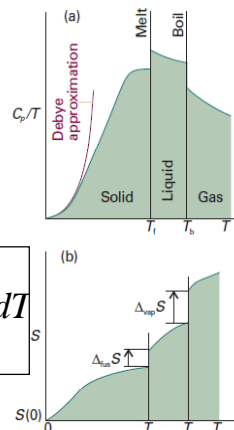
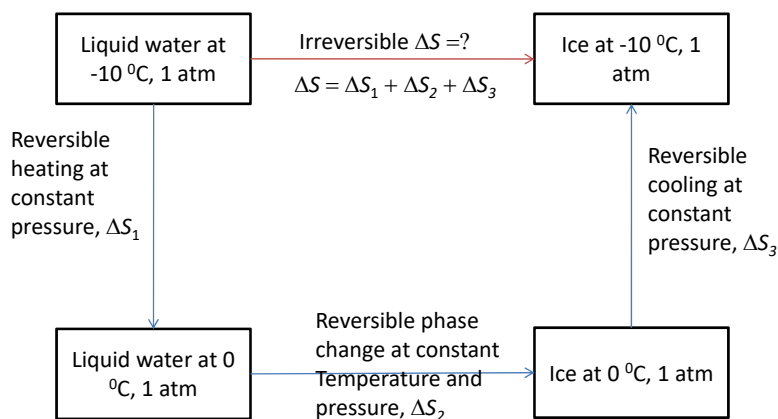


Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

Construction of Reversible Steps to describe an Irreversible Process

Example



Entropy is an extensive property. $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

Entropy of Mixing of ideal gases

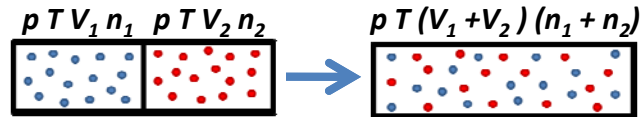
$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}$
 $\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$

Entropy of Mixing of ideal gases

$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$
 $\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}, \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$

$$\frac{V_1}{V_1 + V_2} = \frac{\frac{n_1 R T}{p}}{\frac{n_1 R T}{p} + \frac{n_2 R T}{p}} = \frac{n_1}{n_1 + n_2} = x_1$$

Entropy of Mixing of ideal gases



$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1} \quad \text{and} \quad \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$\begin{aligned} \Delta S_{\text{mix}} &= -n_1 R \ln x_1 - n_2 R \ln x_2 \\ &= -nR(x_1 \ln x_1 + x_2 \ln x_2) \end{aligned}$$

For what value of x_i is ΔS_{mix} maximum?

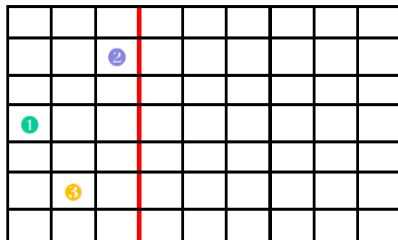
Statistical View of Entropy

The equilibrium thermodynamic state of an isolated system is the most probable state.

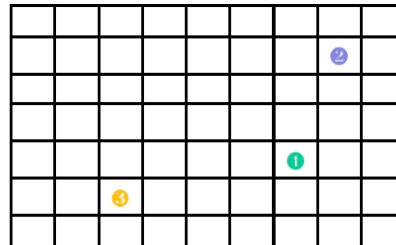
$$S = k_B \ln W$$

k_B is Boltzmann's constant

W is number of different ways in which the energy of the system can be arranged (number of microstates)



$$W = 21 \times 20 \times 19 = 7,980$$



$$W = 63 \times 62 \times 61 = 2,38,266$$

Criteria for spontaneity

$$dS_{\text{sys}} + dS_{\text{surr}} > 0$$

For a closed system, no non p-V (additional) work

$$dU_{S,V} \leq 0$$

$$dH_{S,p} \leq 0$$

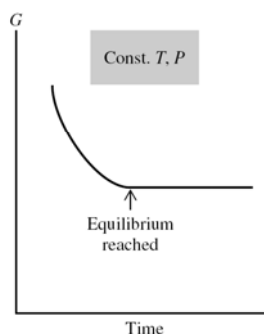
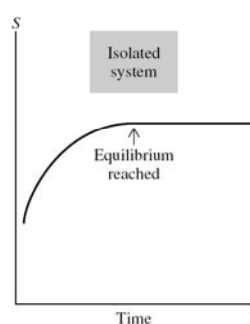
$$dA_{V,T} \leq 0$$

$$dS_{U,V} \geq 0$$

$$dS_{H,p} \geq 0$$

$$dG_{p,T} \leq 0$$

Reversible processes carry equal sign.



Combination of First and Second Laws of Thermodynamics:

$$dU = dw + dq$$

True for any path

$$dU = dw_{\text{rev}} + dq_{\text{rev}}$$

$$dS \geq dq/T$$

$$dS = dq_{\text{rev}}/T$$

$$dU = -pdV + TdS$$

The Fundamental Equation of Thermodynamics

$$\begin{aligned} dA &= d(U - TS) \\ &= dU - TdS - SdT \\ &= -pdV + TdS - TdS - SdT \\ &= -pdV - SdT \end{aligned}$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

The Fundamental Equation of Chemical Thermodynamics

Combination of First and Second Laws of Thermodynamics

Closed system with only pV work

$$dU = -pdV + TdS$$

$$dA = -pdV - SdT$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

Properties of partial derivatives

- 1st order Differential of $f(x, y)$

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

- 2nd order partial derivative of $f(x, y)$

Let $\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial^2 f}{\partial x \partial y} \quad \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) = \frac{\partial^2 f}{\partial y \partial x}$

$$dU = -pdV + TdS$$

$$dA = -pdV - SdT$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

Other forms of energy in thermodynamics

- Enthalpy, $H = U + pV$

$$dH = dU + p dV + V dp = T dS - p dV + p dV + V dp$$

$$dH = T dS + V dp$$

- Helmholtz free energy, $A = U - TS$

$$dA = dU - T dS - S dT = T dS - p dV - T dS - S dT$$

$$dA = -S dT - p dV$$

- Gibbs free energy, $G = U - TS + pV$

$$\begin{aligned} dG &= dU - T dS - S dT + p dV + V dp \\ &= T dS - p dV - T dS - S dT + p dV + V dp \end{aligned}$$

$$dG = -S dT + V dp$$

Formal structure of thermodynamics of an isolated system

The Fundamental equation

$$U = U(S, V, N)$$

$$dU = T dS - p dV$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, N}$$

The Maxwell Relations

$$dU = -pdV + TdS$$

$$dU = \left(\frac{\partial U}{\partial V} \right)_S dV + \left(\frac{\partial U}{\partial S} \right)_V dS$$

$$\left(\frac{\partial U}{\partial V} \right)_S = -p \quad \text{and} \quad \left(\frac{\partial U}{\partial S} \right)_V = T$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

$$\boxed{-\left(\frac{\partial p}{\partial S} \right)_V = \left(\frac{\partial T}{\partial V} \right)_S} \quad \text{Maxwell Relation}$$

$$\boxed{dG = Vdp - SdT}$$

$$\boxed{\left(\frac{\partial G}{\partial p} \right)_T = V}$$

$$\boxed{\left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p} \right)_T \right]_p = \left(\frac{\partial V}{\partial T} \right)_p}$$

$$\boxed{\left(\frac{\partial G}{\partial T} \right)_p = -S}$$

$$\boxed{\left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T} \right)_p \right]_T = -\left(\frac{\partial S}{\partial p} \right)_T}$$

G is a state function and dG is an exact differential.

$$\boxed{\left(\frac{\partial S}{\partial p} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_p}$$

Isothermal variation of
entropy with pressure

Maxwell Relation

The Maxwell Relations

$dG = Vdp - SdT$	$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$	$\left. \begin{array}{l} \\ \end{array} \right\}$ Isothermal variation of entropy with pressure and volume
$dA = -pdV - SdT$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$	
$dU = -pdV + TdS$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$	
$dH = Vdp + TdS$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$	

Determination of $\Delta_r G^0$ and $\Delta_r S^0$

$$\Delta_r H^0 = \sum_{\text{products}} \nu \Delta_f H^0 - \sum_{\text{reactants}} \nu \Delta_f H^0$$

$$\Delta_r S^0 = \sum_{\text{products}} \nu S_m^0 - \sum_{\text{reactants}} \nu S_m^0$$

$$\Delta_r G^0 = \sum_{\text{products}} \nu \Delta_f G^0 - \sum_{\text{reactants}} \nu \Delta_f G^0$$

$$\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0$$

The Maxwell Relations

(a) $\Delta U = q + w$
 (b) $\Delta S = q_{\text{rev}}/T$
 (c) $H = U + pV$
 (d) $A = U - TS$
 (e) $G = H - TS$

$$\left(\frac{\partial T}{\partial V}\right)_S \stackrel{1.}{=} -\left(\frac{\partial p}{\partial S}\right)_V \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T \stackrel{3.}{=} \left(\frac{\partial p}{\partial T}\right)_V \quad \left(\frac{\partial S}{\partial p}\right)_T \stackrel{4.}{=} -\left(\frac{\partial V}{\partial T}\right)_p$$

1. $dU = TdS - pdV$

2. $dH = TdS + Vdp$

3. $dA = -SdT - pdV$

4. $dG = -SdT + Vdp$

$$Mdx + Ndy = dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Properties of the Gibbs energy

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT \longrightarrow G = f(p, T)$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dU = TdS - pdV$$