The Third Law of Thermodynamics

- "If the entropy of every element in its stable state at $T = 0$ is taken as zero, every substance has a _______ entropy which at $T = 0$ may become zero, and does become zero for all perfect _______ substances, including compounds."

- Limiting Heat Theorem: "The entropy change accompanying transformation between condensed phases in equilibrium, including chemical _______ , approaches zero as $T \to 0$.

- Practical consequence: Set $S(0) = 0$ for _______ by convention. Apply Nernst to determine $S(0)$ for all else.

- "It is impossible to reach absolute zero in a _______ number of steps."

The 1st Law says $U$ cannot be _______ or _______ .

The 2nd Law says $S$ cannot _______ .

The 3rd Law says zero _______ cannot be reached.

The Fundamental _______ of Thermodynamics

Combine $dU = \delta q - PdV$ with $dS = \frac{\delta q_{rev}}{T}$ Reversible change but true for all paths since $dV$ exact

or $dS = \left(\frac{T}{\partial U}\right)_V dU + \left(\frac{P}{\partial V}\right)_S dV$ : $\delta w_{rev} = -PdV$

This fundamental equation generates many more _______

Example 1: Comparison with $dU = \left(\frac{\partial U}{\partial V}\right)_T dV$ which is a _______ relation

Example 2: Consider that $dU$ is exact and cross _______.

Example 3: Consider that $dS$ is exact and cross _______.

How Entropy Depends on $T$ and $V$

$\Delta S = \int \frac{C_v}{T} dT$

Compare with $\Delta S_T = \int \frac{P}{T} = \int \frac{1}{V} dV$

For _______ substance,

$\Delta S = \frac{C_v}{T} dT + \frac{\alpha}{\kappa} dV$

For _______ gases, $\Delta S = \frac{C_v}{T} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ assuming $C_v$ is _______ (eqs 3.7.4, 6.1.6)

The ________ Inequality

Given $dS = \frac{\delta q_{rev}}{T}$ and $\delta w_{rev} = -PdV$

Substitute into the 1st Law:

$dU = TdS - PdV$

of Thermodynamics

All _______ differentials, so path independent.

But $dU = \delta q + \delta w = \delta q - P_{ex} dV$

$\Rightarrow dS = \frac{\delta q}{T} + \left( \frac{\delta w}{T} \right) dV$

If $P > P_{ex}$, $dV > 0$; if $P < P_{ex}$, $dV < 0$

$\Rightarrow (P - P_{ex})dV \geq 0$

Clausius Inequality: $dS \geq \frac{\delta q}{T}$ Equal for _______ change

Even more generally,

$dS_{univ} = \left( \frac{T - T_{surr}}{T} \right) dS_{surr} + \left( \frac{P - P_{surr}}{T} \right) dV$

Conditions for: _______ equilibrium _______ equilibrium

The _______ Inequality

All _______ differentials, so path independent.

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Conditions for: _______ equilibrium _______ equilibrium
Entropy Depends on $T$ and $P$ (not in text)

$$dS = \left( \frac{1}{T} \right) dU + \left( \frac{P}{T} \right) dV$$

First problem: replace ____ ; second problem: replace ____.

Use $d____ = dH - Pd____$ and both are solved!

But

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

$$\Rightarrow dS = \frac{C_p}{T} dT + \frac{T}{P} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] dP$$

Compare with

$$dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial P} dP \quad \text{variables}$$

$$\frac{\partial S}{\partial T} = \frac{C_p}{T} \quad \frac{\partial S}{\partial P} = \frac{T}{P} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right]$$

$$\Delta S = \int \frac{C_p}{T} dT$$

$$\Delta S_T = - \int \frac{V}{T} dT = \frac{1}{P} \int dP$$

$$\Delta S_T = -nR \ln \left( \frac{P_2}{P_1} \right) = \ln \left( \frac{V_2}{V_1} \right)$$

Entropy Changes in ________ Processes

Entropy is a ________ function, so

$$\Delta S_{\text{(sys)}} = S_2 - S_1 \quad \text{of path}$$

This can be used to calculate $\Delta S$ for an irreversible process.

1. **Consider isothermal expansion of a gas from $V_1$ to $V_2$:**

   $$\Delta S_{\text{(sys)}} = nR \ln \left( \frac{V_2}{V_1} \right) \quad \text{reversible and irreversible cases}$$

   For the reversible case

   $$\Delta S_{\text{(surr)}} = -\frac{W}{T}$$

   e.g. for ______ expansion, $W = 0$

   $$\Rightarrow \Delta S_{\text{(surr)}} = 0, \quad \Delta S_{\text{(uni)}} = \Delta S_{\text{(sys)}} > 0$$

2. **Consider freezing of ______ water at $T < 273$ K**

   water, 0°C $\rightarrow$ reversible $\rightarrow$ ice, 0°C

   water, $T$ $\rightarrow$ irreversible $\rightarrow$ ice, $T$

   $\Delta S_{\text{(sys)}} = \Delta S_{\text{(surr)}}$

   Using Entropy to Achieve Low $T$

   $$\Delta S_p = \int \frac{C_p}{T} dT \approx C_p \ln \left( \frac{T_2}{T_1} \right) \quad \text{if } C_p \text{ is } \approx \text{constant}$$

   To achieve lower temperatures, $S$ must be reduced.

   Choose some property $X$ that varies with $S$, i.e. $S = f(X, T)$.

   This could be the pressure of a gas or, for example, the magnetic moment of a paramagnetic salt (whose energy varies with magnetic field).

1. Alter $X$ isothermally. $\Delta S_T \approx \left( \frac{\partial S}{\partial X} \right)_T \Delta X, \quad q = T \Delta S$

2. Restore $X$ by a reversible adiabatic process.

3. Repeat cycle.

Entropy of ________

- Consider the mixing of two ideal gases:
  - $P_1, T, V_1, n_1$
  - $P, T, V_2, n_2$

  $\Delta S_1 = -n_1 R \ln \frac{V_1}{n_1 + n_2} = -n_1 R \ln ___ 1$

  $\Delta S_2 = -n_2 R \ln \frac{V_2}{n_1 + n_2} = -n_2 R \ln ___ 2$

  $\Delta S_{\text{mix}} = -n_1 R \ln \chi_1 - n_2 R \ln \chi_2 = -(n_1 + n_2) R (___)$

  In general

  $$\Delta S_{\text{mix}} = -R \sum \chi_i \ln \chi_i$$

This expression applies to the arrangement of objects (________) just as well as (________) (gases and liquids).

For example, arrange $N$ identical atoms in $N$ sites in a crystal:

$$\Omega = N! / N! = ___ \quad S = k \ln \Omega = ___$$

Compare with the arrangement of two types of atoms, A and B:

$$\Omega = \frac{N!}{N_A! N_B!} \quad \Delta S = k (___)$$

Application of ________ approximation: $\ln (z!) = \ln ___ - ___$

leads to $\Delta S_{\text{config}} = -kN (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$ do the math

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