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."

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

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

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 ________ Inequality

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

Substitute into the 1st Law:

$$dU = Td\underline{\quad} - Pd\underline{\quad}$$

________ Equation of Thermodynamics

All ________ differentials, so path independent.

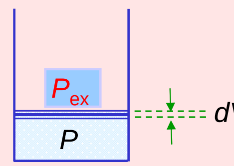
But $dU = \delta q + \delta w = \delta q - P_{\text{ex}}dV$ In general, i.e. any path

$$\underline{\quad\quad} - \underline{\quad\quad} = \delta q - P_{\text{ex}}dV$$

$$\Rightarrow dS = \frac{\delta q}{T} + \frac{(\underline{\quad} - \underline{\quad})}{T}dV$$

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

$$\therefore (P - P_{\text{ex}})dV \geqslant 0$$



Clausius Inequality $dS \geqslant \frac{\delta q}{T}$ Equal for ________ change

Even more generally,

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

Conditions for: ________ equilibrium ________ equilibrium

The Fundamental ________ of Thermodynamics

Combine $dU = \delta q - PdV$ with $dS = \frac{\delta q_{\text{rev}}}{T}$

Reversible change but true for all paths since dV exact

$$\Rightarrow dU = TdS - PdV$$

$\delta w_{\text{rev}} = -PdV$

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

This fundamental equation generates many more ________.

Example 1: Comparison with $dU = \left(\frac{\partial U}{\underline{\quad}}\right)_V \underline{\quad} + \left(\frac{\partial U}{\partial \underline{\quad}}\right)_S \underline{\quad}$

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

Example 2: Consider that dU is exact and cross ________.

use this relation here → $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ which is a ________ relation

Example 3: $\left(\frac{\partial S}{\partial V}\right)_T = \underline{\quad}\left(\frac{\partial S}{\underline{\quad}}\right)_{\underline{\quad}}\left(\frac{\underline{\quad}}{\partial V}\right)_{\underline{\quad}}$ cyclic rule…

$= \underline{\quad}\left(\frac{\partial P}{\underline{\quad}}\right)_{\underline{\quad}}\left(\frac{\underline{\quad}}{\partial T}\right)_{\underline{\quad}} = \left(\frac{\partial P}{\partial T}\right)_V$ …again…

…and again! $= \underline{\quad}\left(\frac{\underline{\quad}}{\partial T}\right)_{\underline{\quad}}\left(\frac{\partial P}{\underline{\quad}}\right)_{\underline{\quad}} = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$

$= \alpha/\kappa$

How Entropy Depends on T and V

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

$dU = \boxed{\quad\quad\quad\quad}$

$$\Rightarrow dS = \frac{C_V}{T}dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

Compare with $dS = \left(\frac{\underline{\quad}}{\underline{\quad}}\right)_{\underline{\quad}} dT + \left(\frac{\underline{\quad}}{\underline{\quad}}\right)_{\underline{\quad}} dV$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

0 for ideal gases

$$\Delta S_{\underline{\quad}} = \int \frac{C_V}{T}dT$$

$$\Delta S_T = \int \frac{P}{T}\underline{\quad} = \underline{\quad}\int \frac{1}{V}dV = nR\underline{\quad}(V_2/V_1)$$

For ______ substance, $dS = \frac{C_V}{T}dT + \frac{\alpha}{\kappa}dV$

For ________ gases, $\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ assuming C_V is T ________

(eqs 3.7.4, 6.1.6)

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 $d\underline{\quad} = dH - Pd\underline{\quad} - VdP$ and both are solved!

$$\Rightarrow dS = \left(\frac{1}{T}\right)dH - \left(\frac{V}{T}\right)dP$$

But $\quad dH = \left(\frac{\partial H}{\underline{\quad}}\right)_P \underline{\quad} + \left(\frac{\partial H}{\underline{\quad}}\right)_T \underline{\quad} = \underline{\quad}\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

$$\Rightarrow dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Compare with $\quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad$ _____ variables

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad\qquad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$\left(\frac{\partial H}{\partial P}\right)_T \to$ 0 for ideal gases

$$\Delta S_{\underline{\quad}} = \int \frac{C_P}{T}dT \qquad\qquad \Delta S_T = -\int \frac{V}{T}\underline{\quad} = -\underline{\quad}\int \frac{1}{P}dP$$

$$\Delta S_T = -nR\underline{\quad}(P_2/P_1) = \underline{\quad}\, nR\ln(V_2/V_1)$$

Entropy Changes in _____ Processes

Entropy is a _____ function, so

$\Delta S(\text{sys}) = S_2 - S_1$ _____ of path

This can be used to calculate ΔS for an irreversible process.

❖ Consider isothermal expansion of a gas from V_1 to V_2:

$$\Delta S(\text{sys}) = nR\ln(V_2/V_1) \quad \text{reversible and irreversible cases}$$

For the reversible case $\quad \Delta S(\text{surr}) = -\Delta S(\text{sys})$

For the irreversible case $\quad \Delta S(\text{surr}) \underline{\quad} -\Delta S(\text{sys})$

$$\Delta S(\text{surr}) = -\frac{q}{T} = \frac{w}{T}$$

e.g. for _____ expansion, $w = 0$

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

❖ Consider freezing of _____ water at T < 273 K

$$\begin{array}{ccc} \text{water, 0°C} & \xrightarrow{\text{reversible}} & \text{ice, 0°C} \\ \text{rev.}\uparrow & & \downarrow\text{rev.} \\ \text{water, } T & \xrightarrow{\text{irreversible}} & \text{ice, } T \end{array}$$

$\Delta S(\text{sys}) =$

$\Delta S(\text{surr}) =$

Entropy of _____

❖ Consider the mixing of two ideal gases :

P, T, V_1, n_1	P, T, V_2, n_2	➡	P, ___ , V_1+V_2, n_1+ ___

$$\Delta S_1 = -n_1R\ln\frac{V_1}{\underline{\quad}} = -n_1R\ln\frac{n_1}{n_1+n_2} = -n_1R\ln\underline{\quad}_1$$

$$\Delta S_2 = -n_2R\ln\frac{V_2}{\underline{\quad}} = -n_2R\ln\frac{n_2}{n_1+n_2} = -n_2R\ln\underline{\quad}_2$$

$$\Delta S_{\text{mix}} = -n_1R\ln\chi_1 - n_2R\ln\chi_2 = -(n_1+n_2)R(\underline{\qquad\qquad})$$

In general $\quad \Delta S_{\text{mix}} = -\underline{\quad}R\sum_i \chi_i\ln\chi_i$

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:

$$\Omega = N!/N! = \underline{\quad} \qquad S = k\ln\Omega = \underline{\quad}$$

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

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

Application of _____ approximation: $\ln(z!) = \underline{\quad}\ln\underline{\quad} - \underline{\quad}$

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

Using Entropy to Achieve Low T

$$\Delta S_P = \int \frac{C_P}{T}dT \approx C_P\ln(T_2/T_1) \qquad \text{if } C_P \text{ is} \approx \text{constant}$$

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. Entropy changes. $\quad \Delta S_T \approx \left(\frac{\partial S}{\partial X}\right)_T \Delta X, \quad q = T\Delta S$
2. Restore X by a reversible adiabatic process. $\quad q = 0, \quad \Delta S = 0$
3. Repeat cycle.