efficiency of a Carnot engine $\varepsilon = 1 + (q_{c,rev}/q_{h,rev}) = 1 - (T_c/T_h)$

$d\boldsymbol{S} \equiv \eth q_{rev}/T$ *Second Law*

$d\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p\, dT + (\partial \boldsymbol{S}/\partial p)_T\, dp$

$d\boldsymbol{S} = (1/T)C_p\, dT - (\partial V/\partial T)_p\, dp$	$d\boldsymbol{S} = (1/T)C_V\, dT + (\partial p/\partial T)_V\, dV$

Third Law:The entropy of a pure, perfectly crystalline substance is zero at the absolute zero of temperature. $\boldsymbol{S}_{0\,K} = 0$

$\boldsymbol{S} = k_B \ln \Omega$

When N particles are indistinguishable from one another, the number of possible arrangements, Ω, of distributing these particles among states having energies $\varepsilon_1, \varepsilon_2, \ldots$ is the number

$$\Omega = N! / \{n_1!\, n_2!\, n_3!\, n_4! \ldots\}$$

where n_1 particles are in ε_1 etc.

entropy of mixing	$\boldsymbol{S} = -k_B N \{x_A \ln x_A + x_B \ln x_B\}$

$d\boldsymbol{U} = Td\boldsymbol{S} - pdV$ general condition of equilibrium, from 1st and 2nd Law

$\Delta \boldsymbol{S} \geq \int \eth q_{irrev}/T$ *Clausius inequality*

in ***isolated system***	$d\boldsymbol{S} \geq 0$

at ***constant T and p***

$\Delta \boldsymbol{G}$ is –	spontaneous change
$\Delta \boldsymbol{G} = 0$	equilibrium
$\Delta \boldsymbol{G}$ is +	natural direction is opposite

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ $\boldsymbol{A} \equiv \boldsymbol{U} - T\boldsymbol{S}$

$d\boldsymbol{G} = (\partial \boldsymbol{G}/\partial T)_p\, dT + (\partial \boldsymbol{G}/\partial p)_T\, dp$	$(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{H}/T^2)$
$d\boldsymbol{G} = Vdp - \boldsymbol{S}dT$	

Define the free energy per mole (***the chemical potential***): $\mu(T) = \boldsymbol{G}(T)/n$

$\mu(T) = \mu^{\ominus}_T + RT \ln (f/1)$ (real gas)	$\ln \dfrac{f}{p} = \int_0^p \dfrac{(Z-1)}{p}\, dp$

$\mathrm{d}\boldsymbol{S} \equiv \text{đ}q_{rev}/T$

efficiency of a Carnot engine

$$\varepsilon = 1+(q_{c,rev}/q_{h,rev}) = 1-(T_c/T_h)$$

$$\mathrm{d}\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p\, \mathrm{d}T + (\partial \boldsymbol{S}/\partial p)_T\, \mathrm{d}p$$

$$\boxed{\mathrm{d}\boldsymbol{S} = (1/T)C_p\, \mathrm{d}T - (\partial V/\partial T)_p\, \mathrm{d}p}$$

$$\boxed{\mathrm{d}\boldsymbol{S} = (1/T)C_V\, \mathrm{d}T + (\partial p/\partial T)_V\, \mathrm{d}V}$$

3rd Law:The entropy of a pure, perfectly crystalline substance is <u>zero</u> at the absolute zero of temperature. $\boldsymbol{S}_{0\,\mathrm{K}} = 0$

$$\boldsymbol{S} = k_B \ln \Omega$$

When N particles are indistinguishable from one another, the number of possible arrangements, Ω, of distributing these particles among states having <u>energies</u> $\varepsilon_1, \varepsilon_2, \ldots$ is the number

$$\Omega = N! / \{n_1!\, n_2!\, n_3!\, n_4! \ldots\}$$

where n_1 particles are in ε_1 etc.

$$\boxed{\boldsymbol{S} = -k_B N \{ x_A \ln x_A + x_B \ln x_B \}}$$

$d\boldsymbol{U} = T d\boldsymbol{S} - p dV$ general condition of <u>equilibrium</u>, from 1st and 2nd Law

$\Delta \boldsymbol{S} \geq \int đq_{irrev}/T$ *Clausius inequality*

$d\boldsymbol{S}_{\text{isolated system}} > 0$

in ***isolated system***

$$\boxed{T d\boldsymbol{S} \geq 0}$$

at ***constant T and p***

$\Delta \boldsymbol{G}$ is –	spontaneous change
$\Delta \boldsymbol{G} = 0$	equilibrium
$\Delta \boldsymbol{G}$ is +	natural direction is opposite

$$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$$
$$\boldsymbol{A} \equiv \boldsymbol{U} - T\boldsymbol{S}$$

$$\mathrm{d}\boldsymbol{G} = (\partial \boldsymbol{G}/\partial T)_p\, \mathrm{d}T + (\partial \boldsymbol{G}/\partial p)_T\, \mathrm{d}p$$

$$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$$

$$\boxed{(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{H}/T^2)}$$

Define the free energy per mole (***the chemical potential***):

$$\mu(T) = \frac{\boldsymbol{G}(T)}{n}$$

$$\boxed{\mu(T) = \mu^{\ominus}_T + RT \ln \frac{f}{1} \quad \text{(real gas)}}$$

$$\boxed{\ln \frac{f}{p} = \int_0^p \frac{(Z-1)}{p}\, \mathrm{d}p}$$

while calculating entropy, i know that it is a state function, so even if a process is irreversible, we can find the entropy for a reversible process with same initial and final conditions and calculate it. but when we do this, do we have to leave other conditions same??? what i mean is, if the given process is adiabatic, and reversible, then as q = 0, we get change in entropy = 0. however if we consider another process, with the same initial and final conditions, but which is not adiabatic, then we would get a different value of entropy change. so how do we deal with adiabatic reversible processes?

Answer:

Make a clear distinction between "state of the system" and "process" or "path". Do not get mixed up between the concept of “state of the system” and “processes” or “paths” that take a system from one state to another.

The **state of the system** is defined by stating its properties (*p*,*T*, number of moles, ..).
An infinite number of processes can be imagined that will take the system from state $\mathcal{A}$ (with properties $p_{\mathcal{A}}$, $T_{\mathcal{A}}$,...) to another state $\mathcal{B}$ (with properties $p_{\mathcal{B}}$, $T_{\mathcal{B}}$, ...). At least some of the infinite number of possibilities are a single step irreversible, or any number of multi-step processes which combine for example isothermal, constant volume, expansion into a vacuum, adiabatic reversible, adiabatic irreversible, etc., etc. Changes in the state functions (such as *p* or *U* or *H* or *S*) are determined only by the values of the state functions at the two states $\mathcal{A}$ and $\mathcal{B}$. Thus,
$\Delta p = p_{\mathcal{B}} - p_{\mathcal{A}}$, $\Delta V = V_{\mathcal{B}} - V_{\mathcal{A}}$, $\Delta U = U_{\mathcal{B}} - U_{\mathcal{A}}$,
$\Delta H = H_{\mathcal{B}} - H_{\mathcal{A}}$, ... which do not depend on which process took the system from $\mathcal{A}$ to $\mathcal{B}$.

q is not a property of the system, and it is not a state function, therefore it will be different depending on exactly how the system got from $\mathcal{A}$ to $\mathcal{B}$. “Reversible process” is not a property, it is a type of process.

It can be proved, as we have done in class, that some changes in state functions are related to heat that would pass through the boundary between the system and the surroundings. Therefore, experimentally conducting the state change via that very specific path would reveal directly the change in the state function. That is why those particular paths are especially noted in your book. Examples are $\Delta H = q_p$ and $\Delta U = q_V$. Of course, if the initial and final volume of the system are not identical, we can not find out ΔU in this way! And if the initial and final pressure of the system are not identical, we can not find out ΔH in this way!

You have to keep the definition of a quantity in mind every time you use that quantity. Definitions, if stated correctly to start with, do not change from one problem to the next and are therefore not only worthwhile to remember but are absolutely necessary to understand anything in this class.