VIVEKANANDA COLLEGE

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NAAC ACCREDITED ‘A’ GRADE

Topic: Clasius Inequality

Course Title: Chemistry (Gen.)

Paper: GE-2/CC-2

Semester: 2(Gen.)

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CLAUSIUS INEQUALITY AND ENTROPY

– with a little history thrown in.

CARNOT PROPOSED THAT HEAT MUST ALWAYS BE WASTED IN ORDER FOR A HEAT ENGINE TO PRODUCE NET WORK, BUT HE DID NOT QUANTIFY HOW MUCH HEAT HAD TO BE WASTED.

IN ~ 1850 **RUDOLF CLAUSIUS** CONFIRMED THE EXISTING THEORIES:

1. ENERGY IS CONSERVED (1^{ST} LAW) WAS QUANTIFIED AS $Q - W = \Delta U$
2. HEAT FLOWS NATURALLY FROM HOT TO COLD (NOT QUANTIFIED)

AND ADDED AN IMPORTANT CONTRIBUTION:

CLAUSIUS KNEW THAT SOME HEAT HAD TO BE REJECTED FROM A REVERSIBLE (CARNOT) HEAT ENGINE (Q_L), AS CARNOT PROPOSED, AND HE KNEW THAT

$$Q_L = W_{net} - Q_H \qquad (1^{ST} \text{ LAW})$$

BUT NO PRINCIPLE FIXED THE ABSOLUTE AMOUNT OF REJECTED HEAT.

CLAUSIUS THEN OBSERVED THAT FOR REVERSIBLE HEAT ENGINES, THE RATIO OF THE HEAT INPUT TO THE REJECTED HEAT WAS CONSISTENTLY EQUAL TO THE RATIO OF THE ABSOLUTE TEMPERATURES OF THE HIGH AND LOW TEMPERATURE RESERVOIRS:

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \qquad (1)$$

If and only if the temperature of the high (T_H) and low (T_L) temperature reservoirs are always expressed in degrees Kelvin.

REARRANGING (1) FOR A <u>REVERSIBLE HEAT ENGINE</u>:

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \qquad (2)$$

CLAUSIUS THEN EXAMINED <u>IRREVERSIBLE PROCESSES AND FOUND THAT THE RELATION (2) DID NOT HOLD</u>. HE REASONED, FOR EXAMPLE, IF 10 JOULES 0F HEAT FLOW FROM A HOT OBJECT AT 350K INTO A COOL ROOM AT 300K, THEN THE HEAT TRANSFER TERM FOR HEAT LEAVING THE OBJECT AND HEAT TRANSFERRED INTO THE ROOM IS THE SAME AND

$$\frac{Q}{T_H} < \frac{Q}{T_L} \text{ or } \frac{10}{350} < \frac{10}{300} \qquad (3)$$

That is, for irreversible processes, the ratio of heat over absolute temperature <u>increases</u> in the direction of natural heat flow.

COMBINING (2) AND (3) FOR A HEAT ENGINE WITH ONE HEAT INPUT AND ONE HEAT OUTPUT:

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0 \qquad (4)$$

OR FOR ANY SEQUENCE OF PROCESSES WITH DISCRETE HEAT TRANSFER TERMS:

$$\sum_{K}\left(\frac{Q}{T}\right)_{K} \leq 0 \qquad (5)$$

WHERE $\left(\frac{Q}{T}\right)_{K}$ = THE RATIO OF THE AMOUNT OF HEAT TRANSFERRED IN A PROCESS TO THE TEMPERATURE OF THE SURROUNDINGS WHERE HEAT IS TRANSFERRED

CALCULATING THE RATIO AS THE INTEGRAL OF A CONTINUOUS FUNCTION OF $\frac{\delta Q}{T}$, CLAUSIUS' PRINCIPLE FOR A REVERSIBLE OR IRREVERSIBLE <u>CYCLE</u> IS:

$$\oint\left(\frac{\delta Q}{T}\right) \leq 0 \qquad (6)$$

FOR REVERSIBLE CYCLES:

$$\oint\left(\frac{\delta Q}{T}\right) = 0 \quad \text{and} \quad \sum_{K}\left(\frac{Q}{T}\right)_{K} = 0 \qquad (7)$$

FOR IRREVERSIBLE CYCLES:

$$\oint\left(\frac{\delta Q}{T}\right) < 0 \quad \text{and} \quad \sum_{K}\left(\frac{Q}{T}\right)_{K} < 0 \qquad (8)$$

The ratio of heat to temperature has characteristics of a property, since it does not change in a cycle, but it is also associated with heat transfer (a path function). In a paper published in 1865, *"On various forms of the laws of thermodynamics that are convenient for applications,"* Clausius named the heat:temperature ratio **entropy**, from the Greek word for "transformation" with the symbol for entropy, the letter "**S**." Clausius' 1865 paper ends with a bold statement that is the broadest possible application of the laws of thermodynamics:

1. **The energy of the universe is constant (1st Law)**
2. **The entropy of the universe tends toward a maximum (2nd Law)**

Clausius' statement of the 2nd Law of Thermodynamics and his discovery of entropy as the ratio of two macroscopic components: heat and absolute temperature, was truly remarkable since the true nature of entropy was only discovered later when physicists understood the nature of individual atoms and molecules – the microscopic world.

It was the physicist **Ludwig Boltzmann** who in 1905 proposed that the nature of entropy is related to the probability of the state of the atoms or molecules in a system. That is, if the order or arrangement of molecules is unique – has a low probability – then the entropy is low. In contrast, there are many possible combinations of arrangements to obtain a disorderly system – with a high probability – then the entropy is high. For example, if a deck of cards were arranged with the four suits separated and ordered ♣-♦-♥-♠ and all the cards in each suit in ascending sequence (A-K), the arrangement is unique, the probability of accidentally achieving such an arrangement is very low, and the entropy is very low. However, for disorderly arrangements of the cards (suits not in order, cards not in sequence), there are an increasing number of ways to achieve increasingly random arrangements and the entropy increases correspondingly. **Boltzmann's complete explanation of entropy**:

1. **Qualitatively, entropy is disorder, which has a natural tendency to increase.**
2. **Entropy is measured by the ratio of heat to absolute temperature.**
3. **Entropy is theoretically related to the size (number of digits) in the probability space for the arrangement of atoms/molecules in a system.**

It follows from Boltzmann's contribution, that the entropy of a pure crystalline substance at T = 0 K (absolute zero) is zero – no random arrangement. (Sometimes called the 3rd Law of Thermodynamics.)

From Clausius' principle, for an **INTERNALLY REVERSIBLE PROCESS, ENTROPY IN A CLOSED SYSTEM IS:**

$$dS = \frac{\delta Q}{T}$$

$$\int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$ **for reversible processes (9)**

for an **IRREVERSIBLE PROCESS, ENTROPY IN A CLOSED SYSTEM IS:**

$$dS > \frac{\delta Q}{T}$$

$$\int_1^2 dS = S_2 - S_1 > \int_1^2 \frac{\delta Q}{T}$$

defining $\mathbf{S_{gen}}$ **as the entropy generated in the surroundings**, as the difference: $\left(\frac{\delta Q}{T}\right)_{irreversible} - \left(\frac{\delta Q}{T}\right)_{reversible}$ so $\mathbf{S_{gen} > 0}$ **for irreversible processes:**

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$ **for irreversible processes (10)**

Special cases for equation (10):

1. **Reversible processes**

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

2. **Adiabatic processes**

$$S_2 - S_1 = S_{gen}$$

3. **Reversible AND Adiabatic processes are ISENTROPIC**.

$$S_2 - S_1 = 0$$

ENTROPY IN OPEN SYSTEMS (CONTROL VOLUME)

$$\frac{dS_{cv}}{dt} = \sum_k \left(\frac{\dot{Q}}{T}\right)_k + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{gen}$$

In **steady-state conditions**, $\frac{dS_{cv}}{dt} = 0$ and

$$\sum_e \dot{m}_e s_e - \sum_i \dot{m}_i s_i = \sum_k \left(\frac{\dot{Q}}{T}\right)_k + \dot{S}_{gen} \qquad (11)$$

Special Cases for equation (11) for control volumes (open systems):

1. For an **open system with a single inlet and outlet at steady-state**:

$$\dot{m}(s_e - s_i) = \sum_k \left(\frac{\dot{Q}}{T}\right)_k + \dot{S}_{gen}$$

2. For an **adiabatic process in an open system at steady-state with single inlet and outlet**:

$$\dot{m}(s_e - s_i) = \dot{S}_{gen}$$

3. for a **reversible process in an open system at steady-state with single inlet and outlet:**

$$\dot{m}(s_e - s_i) = \sum_k \left(\frac{\dot{Q}}{T}\right)_k$$

4. **for an adiabatic and reversible process in an open system at steady-state (isentropic process)**

$$s_e - s_i = 0$$

ENTROPY FOR A CYCLE: $\Delta S = 0$ and

$$\dot{S}_{gen} = -\sum_k \left(\frac{\dot{Q}}{T}\right)_k$$

UNITS OF ENTROPY:

intensive property, s: $\frac{\text{kJ}}{\text{kg} - \text{K}}$

extensive property, S: $\frac{\text{kJ}}{\text{K}}$

rate of entropy change/transfer: $\dot{m}s = \dot{S} : \frac{\text{kw}}{\text{K}}$

SIGN CONVENTION FOR S IS THE SAME AS FOR HEAT.

IF HEAT IS TRANSFERRED INTO THE SYSTEM ($Q > 0$) THEN THE ENTROPY OF THE SYSTEM INCREASES ($\Delta S > 0$).

IF HEAT IS TRANSFERRED OUT OF THE SYSTEM ($Q < 0$) THEN THE ENTROPY OF THE SYSTEM MUST DECREASE ($\Delta S < 0$).

Results of entropy:

A. Equilibrium can be defined as a state of maximum entropy of an isolated system, and spontaneous changes only occur in the direction of increasing entropy of the universe (S_{gen}).
B. Entropy is NOT conserved in real (irreversible processes).
C. The magnitude of generated entropy is proportional to the magnitudes of irreversibilities.