

## Properties of Entropy

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Due to its additivity, **entropy is a homogeneous function** of the extensive coordinates of the system:

$$S(\lambda U, \lambda V, \lambda N_1, \dots, \lambda N_m) = \lambda S(U, V, N_1, \dots, N_m)$$

This means we can **write the entropy as a function** of the total number of particles and **of intensive coordinates: mole fractions and molar volume**

$$\text{If } \lambda = 1/N$$

$$N S(u, v, n_1, \dots, n_m) = S(U, V, N_1, \dots, N_m)$$

$$\sum n_i = 1$$

## *Intensive Thermodynamic Coordinates*

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The fundamental relation in the energy representation gives the internal energy of the system as a function of all extensive coordinates (including the entropy)

$$U = U(S, V, N_1, \dots, N_m)$$

Since the internal energy is a **function of the state of the system**, we can write its first **differential** as:

$$dU = (\partial U / \partial S)_{V, N_1, \dots, N_m} dS + (\partial U / \partial V)_{S, N_1, \dots, N_m} dV + (\partial U / \partial N_1)_{S, V, N_2, \dots, N_m} dN_1 + \dots$$

The **partial derivatives** in this differential are **functions** of the same extensive parameters as the internal energy.

## New Intensive Thermodynamic Variables

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It is convenient to give names to these partial derivatives:

$$(\partial U / \partial S)_{V, N_1, \dots, N_m} = T, \quad \text{temperature}$$

$$- (\partial U / \partial V)_{S, N_1, \dots, N_m} = P, \quad \text{pressure}$$

$$(\partial U / \partial N_1)_{V, S, N_2, \dots, N_m} = \mu_1 \quad \text{electrochemical potential}$$

We will show that the properties of the above defined variables coincide with our intuitive understanding of temperature, pressure and chemical potential

$$dU = (\partial U / \partial S)_{V, N_1, \dots, N_m} dS + (\partial U / \partial V)_{S, N_1, \dots, N_m} dV + (\partial U / \partial N_1)_{S, V, N_2, \dots, N_m} dN_1 + \dots$$



$$dU = T dS - P dV + \mu_1 dN_1 + \dots$$



$$dS = (1/T) dU + (P/T) dV - (\mu_1/T) dN_1 + \dots$$

## *Relation between Entropy and Heat*

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If the number of particles is constrained in a given process ( $dN = 0$ ):

$$dU = T dS - P dV$$

On the other hand, we have conservation of energy:

$$dU = \delta W + \delta Q$$

Since work is:  $\delta W = - P dV$ , we find the connection between heat and entropy:

$$\delta Q = T dS$$

*Flux of heat into the system increases its entropy.*

## *Equations of State*

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The intensive parameters we just introduced written as functions of the extensive parameters are called the **equations of state**:

$$T = T(S, V, N_1, \dots, N_m)$$

$$P = P(S, V, N_1, \dots, N_m)$$

$$\mu_i = \mu_i(S, V, N_1, \dots, N_m)$$

## *Equations of State*

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The equations of state connect coordinates of thermodynamic systems to each other.

This means that not all thermodynamic coordinates are independent!

A **full set of the equations of state** carries the **same information** about a thermodynamic system as the **fundamental relation**.

If experimentally determined, the equations of state can be used to reconstruct the functional form of the fundamental relation by integration of **dU** or **dS**. We will consider a few examples of such constructions.

# Temperature

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In *equilibrium*, the entropy of the **system + its environment** has a maximum as a function of all unconstrained coordinates of the system and environment, therefore

$$dS = dS_1 + dS_e = 0$$

for variations of **any** unconstrained extensive coordinate **in equilibrium**.

Let us consider **variation** of the **internal energy U** of the system and its environment (a situation when only **U** is unconstrained):

$$dS = (\partial S / \partial U_1)_{V, N_1, \dots, N_m} dU_1 + (\partial S / \partial U_e)_{V, N_1, \dots, N_m} dU_e = 0$$

Or, using the definition of temperature:  $dS = 1/T_1 * dU_1 + 1/T_e * dU_e = 0$

# Temperature

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$$dS = 1/T_1 * dU_1 + 1/T_e * dU_e = 0$$

Using the fact that the total energy of the **composite isolated super-system**  $U = U_1 + U_e$  is conserved:

$$dU = dU_1 + dU_e = 0 \quad \longrightarrow \quad dU_1 = - dU_e$$

We obtain:  $dS = (1/T_1 - 1/T_e) dU_1 = 0 \quad \longrightarrow \quad T_1 = T_e$  (since  $dU_1 \neq 0$ )

Temperatures of the system and its environment are the same if **U** is unconstrained !



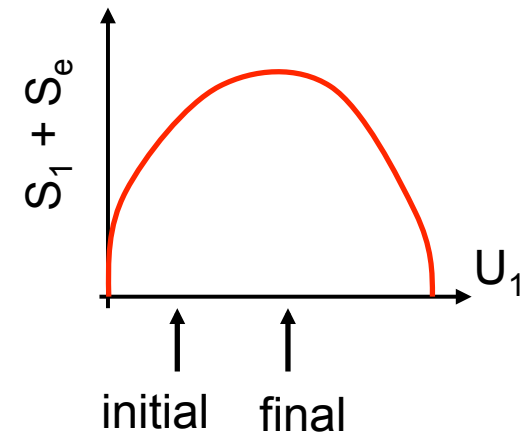
## Temperature difference and the direction of heat flow

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Let us consider a system initially adiabatically insulated from the environment. Temperatures of the system and environment can be initially different  $T_1 > T_e$ .

If we remove the adiabatic constraint, energy will flow between the system and its environment and the entropy will increase in the new equilibrium state (find a new maximum):  $dS > 0$  (Postulate II).

$$dS = (1/T_1 - 1/T_e) * dU_1 > 0$$



Since  $T_1 > T_e$ ,  $dU_1 < 0$ . Therefore, heat will flow from the hot to the cold system. This is consistent with our intuitive notion of temperature.

## Temperature : Units

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Since  $S$  is a monotonically increasing function of  $U$  (Postulate III), temperature  $T = (\partial U / \partial S)_{V, N_1, \dots, N_m}$  is never negative.

Postulate IV also tells us that at zero temperature, entropy is zero, so zero temperature is in principle possible.

Therefore, the minimum possible temperature in thermodynamics is zero.

Thus, any temperature scale that uses negative temperatures cannot serve as a thermodynamic temperature scale

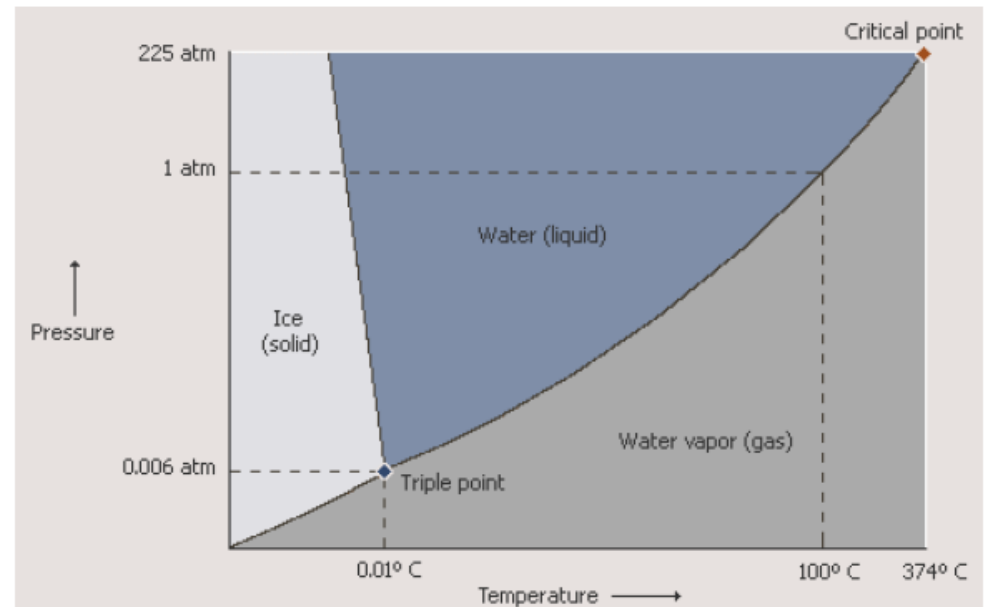
The thermodynamic, absolute (Kelvin) temperature scale has  $T = 0$  when  $S = 0$ . The unit of the temperature scale is Kelvin.

## The Absolute Temperature Scale

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The **absolute (Kelvin) temperature scale** is based on assigning a definite value of  $T$  to the triple point for **water** (at  $T=273.16\text{K}$  and  $P = 611.73\text{Pa}$  water can coexist in the solid, liquid, and gas forms in equilibrium).

The **triple point of water is unique**, and has a unique temperature  $T = 273.16\text{K}$ .



## Temperature and Entropy: Units

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Since  $\delta Q = TdS$ , the product of entropy and temperature should have the dimensions of energy.

- Since entropy is just the logarithm of the number of microscopic states, it is natural to make it a dimensionless quantity
- In this case, temperature should have units of energy
- A thermodynamic unit for temperature is Kelvin (K). Kelvins can be converted into Joules via the Boltzmann constant:  $E = k_B T$  ( $k_B = 1.38 \cdot 10^{-23} \text{ J/K}$ ). It would be great if temperature was measured in yoctoJoules ( $1 \text{ yJ} = 10^{-24} \text{ J} = 13.8 \text{ K}$ ).
- SI defines temperature to be 273.16 K at the equilibrium state of ice, water and water vapor coexistence.