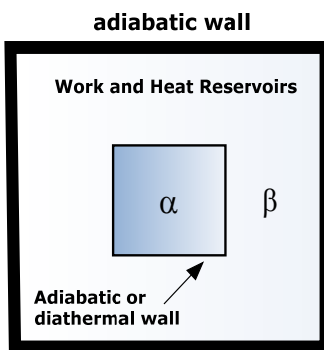


CALCULATION OF THE ENTROPY FOR AN ARBITRARY PROCESS

By definition, the entropy S is defined in terms of reversible processes only, whereas real processes are always irreversible; so the question is, how do we calculate the entropy of an arbitrary irreversible process?

In the following diagram, we imagine an adiabatically isolated 'composite' which contains within it the **surroundings β** , and the **system α** , which is separated from β by an adiabatic or diathermal wall. The surroundings, β of the composite are composed of work and heat reservoirs of an infinite extent and at constant volume so that the properties of the surroundings (eg, the temperature) do not change when β interacts with α . The surroundings, β , are sometimes called the 'universe' but we don't need anything that grandiose – in fact, the surroundings are often nothing more than a simple constant temperature bath containing the system which itself may be a glass vessel containing a reaction mixture. The glass is then the diathermal wall separating α and β . The constant temperature bath might or might not be adiabatically shielded.



Second Law

Using our imagined concept of an adiabatically isolated 'composite', we can write,

$$dS_{\text{total}} = dS_{\text{sys}} + dS_{\text{surr}} \equiv dS^{\alpha} + dS^{\beta} \quad \text{for the composite}$$

The second law then states:

If a process occurs in an 'isolated composite', then

$$dS_{\text{total}} \geq 0 \quad \text{where} \quad \begin{cases} > \text{ implies a spontaneous irreversible process} \\ = \text{ implies a reversible process, i.e., equilibrium} \\ < 0 \text{ implies an impossible process} \end{cases}$$

Thus dS_{total} can serve as a general criterion for irreversible change. Note that dS_{sys} and dS_{surr} can have any sign as long as the total is positive. The only problem is that in order to use dS_{total} as a criterion for say, determining if an arbitrary reaction can actually occur spontaneously is that dS_{surr} is generally difficult or often impossible to calculate. That is why we preferably use $dG_{T,P}$ or $dA_{T,P}$ for this purpose since all of the terms in these functions refer to the system only, and not the surroundings. The price we pay for this convenience however is the loss of generality because of the restrictions of constant T , P or V .

This then brings us to the question of just how we actually calculate ΔS^{α} and ΔS^{β} in order to get ΔS_{total} . We start with the system entropy.

System Entropy Change

Here we devise a **reversible** analog or model of the actual process which connects the final and initial states of the system. Since dS is exact then dS (reversible model) = dS (actual process). Note that the reversible model need not have anything in common with the actual process except the same initial and final states!

We then compute $\Delta S^\alpha = \int \frac{dQ_{rev}^\alpha}{T^\alpha}$ where dQ_{rev}^α is the reversible heat transferred to or from the system at the

temperature T^α **FOR THE REVERSIBLE MODEL**, not the actual process. For closed systems that depend on only P, V and T we can use any of the following relationships for the **SYSTEM**. Be sure you know how to derive these equations!

$$dS^\alpha = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dS^\alpha = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$dS^\alpha = \frac{C_v}{T} \left(\frac{\partial T}{\partial P} \right)_V dP + \frac{C_p}{T} \left(\frac{\partial T}{\partial V} \right)_P dV$$

$$\Delta S^\alpha = \frac{\Delta_{\text{phase1}}^{\text{phase2}} H_{\text{Trans}}}{T_{\text{Trans}}} \quad \text{Phase Transitions}$$

Surroundings Entropy Change

This is a bit trickier. To begin with, assume the walls surrounding the **system** are diathermal so the system can exchange heat with the surroundings. Remember the walls surrounding the composite are adiabatic and rigid and that the heat reservoir part of the surroundings has an infinite heat capacity so that T^β is constant no matter how much heat is exchanged with α . We also assume the 'work reservoir' has an infinite capacity in the sense that the surroundings do not change irrespective of how much work is done on or by the system. From the first law we have:

$$dU^\beta = dQ^\beta + dW^\beta = dQ^\beta \quad \text{because } dW^\beta = 0 \text{ due to the constant volume property of } \beta.$$

This means dQ^β is a state function i.e., dQ^β is exact because dU^β is exact, which in turn implies,

$$1) \quad dQ^\beta (\text{rev}) = dQ^\beta (\text{actual})$$

in other words, the **actual** amount of heat exchanged between the system and the surroundings is the same irrespective as to how the process was carried out, i.e., reversibly or irreversibly. That is, from the viewpoint of the surroundings, it does not matter if the process is reversible or irreversible because the amount of heat transferred depends only on the end points of the process.

Now, the composite has an adiabatic wall so

$$2) \quad dQ (\text{composite}) = dQ^\beta (\text{actual}) + dQ^\alpha (\text{actual}) = 0$$

where we note that we are talking about the **actual** process, not the **model** process for the system!

From 2) we have

dQ^β (actual) = - dQ^α (actual) or, on using 1) above, we have,

dQ^β (rev) = - dQ^α (actual) which is the result we are after

So finally we can write, using the formal definition of the entropy,

$$\Delta S^\beta \equiv \int \frac{dQ_{rev}^\beta}{T^\beta} = - \int \frac{dQ_{actual}^\alpha}{T^\beta}$$

which is a splendid result for now we can, in principle at least, calculate dQ_{actual}^α using the first law for the **system**, not the **surroundings**. Thus, we have a recipe for calculating the entropy change in the surroundings by asking ourselves 'how much heat was actually transferred between α and β in the REAL process' and at what temperature? Then, if you are able to calculate the ratio, $\frac{dQ_{actual}^\alpha}{T^\beta}$ you can calculate ΔS^β .

Comments

- If the **system** has an adiabatic wall and the process is irreversible then $dQ_{actual}^\alpha = 0$ so $dS_{surr} = 0$ so now $dS_{total} = dS_{system} \geq 0$ because $dQ_{rev\ model}^\alpha \neq 0$. Remember, the reversible model and the actual process share only the end points of the process – otherwise the two processes will always be quite different physically!
- If the **system** has a diathermal wall and the process is irreversible then neither dS_{sys} or dS_{surr} will be zero and their sum will be > 0 . Note that either entropy can be negative, but not both.
- If the actual process is **reversible** and the system wall is diathermal so $T^\beta = T^\alpha$, then

$$dS^\alpha = \frac{dQ_{rev}^\alpha}{T^\alpha}$$

$$dS^\beta = - \frac{dQ_{actual}^\alpha}{T^\beta} = - \frac{dQ_{rev}^\alpha}{T^\alpha}$$

and $dS_{total} = 0$

- Likewise, if the actual process is **reversible** and the system wall is adiabatic, then, as we have seen above,

$dS^\beta = 0$ and

$$dS^\alpha = \frac{dQ_{rev}^\alpha}{T^\alpha} = 0 \text{ because } dQ_{rev}^\alpha = 0 \text{ so again } dS_{total} = 0$$

The point is, reversible processes are indistinguishable from equilibrium so $dS_{total} = 0$ always, as the 2nd law asserts.