

12.4: Measuring the Entropy Change for Any Reversible Process

We define entropy in terms of its differential as

$$dS = dq^{rev}/T.$$

To measure an entropy change using this definition requires that the process be reversible, which means that the system and surroundings must be at the same temperature as the heat transfer occurs. We understand reversible heat transfer to be the limiting case in which the temperature difference between system and surroundings becomes arbitrarily small. Here we want to consider the conceptual problems associated with keeping the temperature of the surroundings arbitrarily close to the temperature of the system while the system undergoes an arbitrary reversible change, which may include a temperature change.

We can illuminate one necessary aspect by posing a trivial dilemma: Since system and surroundings jointly comprise the universe, the requirement that system and surroundings be at the same temperature might seem to require that the entire universe be at a single temperature. Plainly, this condition is not met; the temperature of the universe varies from place to place. In fact, the requirement is only that the system and that portion of the surroundings with which the system exchanges heat be at the same temperature. We can satisfy this requirement by permitting the exchange of heat between the system and a portion of the surroundings, under conditions in which the combination of the two is thermally isolated from the rest of the universe.

The non-trivial aspect of this problem arises from the requirement that the temperature of the surroundings remain arbitrarily close to the temperature of the system, while both temperatures change and heat is exchanged between the system and the surroundings. A clumsy solution to this problem is to suppose that we exchange one set of surroundings (at temperature T) to a new set (at temperature $T + \Delta T$) whenever the temperature of the system changes by ΔT . A more elegant solution is to use a machine that can measure the entropy change associated with an arbitrary reversible change in any closed system. This is a conceptual device, not a practical machine. We can use it in *gedanken* experiments to make arbitrarily small changes in the temperature and pressure of the system along any reversible path. At every step along this path, the entropy change is

$$dS = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

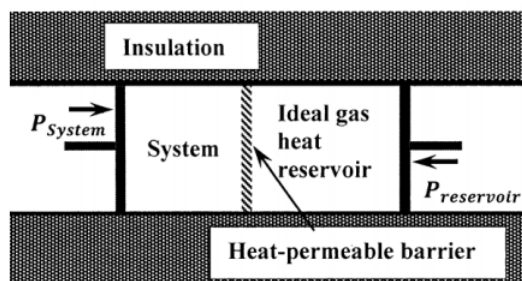


Figure 1. An entropy-measuring machine.

The entropy-measuring machine is sketched in Figure 1. In this device, the portion of the surroundings with which the system can exchange heat is a quantity of ideal gas, which functions as a heat reservoir. This heat reservoir is in thermal contact with the system. The combination of system and ideal-gas heat reservoir is thermally isolated from the rest of the universe. We consider the case in which only pressure–volume work can be done on either the system or the ideal-gas heat reservoir. In this device, all changes are driven by changes in the pressures applied to the surroundings (the ideal-gas heat reservoir) and the system. The pressure applied to the system and the pressure applied to the ideal-gas heat reservoir can be varied independently. We suppose that the system is initially at equilibrium and that changes in the applied pressures are effected in such a manner that all changes in the system and in the ideal-gas heat reservoir occur reversibly. For any change effected in the entropy-measuring machine, the heat and entropy changes in the heat reservoir are \hat{q} and $\Delta\hat{S}$.

Isothermal Process

Let us consider first a process in which a quantity of heat must be transferred from the surroundings to the system while both are at the constant temperature T_P . To be specific, let this be a process in which a mole of pure liquid vaporizes at constant pressure, taking up a quantity of heat equal to the molar enthalpy of vaporization. We can supply this heat by reversibly and isothermally compressing the ideal-gas heat reservoir. To keep the temperature of the ideal-gas heat reservoir constant, we reversibly withdraw

the piston that controls the pressure of the system, causing the vaporization of liquid in the system and absorption by the system of the heat given up by the ideal-gas heat reservoir. Overall, we apply forces to the two pistons to achieve reversible isothermal compression of the ideal gas in the heat reservoir and reversible isothermal vaporization of a quantity of liquid in the system. Because $q = -\hat{q}$, the magnitude of the entropy change for the surroundings is equal to that for the ideal-gas heat reservoir. The entire process is reversible, the entropy change for the system and the entropy change for the surroundings sum to zero: $\Delta S + \Delta \hat{S} = 0$.

We can calculate the entropy change for the ideal-gas heat reservoir. Overall, the \hat{n} moles of ideal gas in the heat reservoir go from the state specified by \hat{P}_1 and T_P to the state specified by \hat{P}_2 and T_P . From the general relationship, $dS = T^{-1}(\partial H/\partial T)_P dT - (\partial V/\partial T)_P dP$, with $dT = 0$, we have $d\hat{S} = -(\hat{n}R/P) dP$ and

$$\Delta \hat{S} = -\hat{n}R \ln \frac{\hat{P}_2}{\hat{P}_1} = \hat{n}R \ln \frac{\hat{V}_2}{\hat{V}_1}$$

The entropy change for the system is $\Delta S = -\Delta \hat{S}$. So long as we carry out the process isothermally and reversibly, we can determine the entropy change for the system simply by measuring the initial and final pressures (or volumes) of the ideal-gas heat reservoir.

Any Reversible Process

If the system undergoes a reversible change in which the temperature of the system is not constant, we can operate the entropy-measuring machine in essentially the same manner as before. The only difference is that we must adjust the pressure applied to the system so that the system temperature changes in the manner required to keep the process reversible—that is, to maintain the system at equilibrium. Then the change to the system and the change to the ideal-gas heat reservoir both take place reversibly. Even though the temperatures change, appropriate control of the applied pressures assures that the system is always in an equilibrium state and that the temperature of the system is always arbitrarily close to the temperature of the ideal-gas heat reservoir.

We can calculate the entropy change for the ideal-gas heat reservoir. Overall, the \hat{n} moles of ideal gas in the heat reservoir go from the state specified by \hat{P}_1 and \hat{T}_1 to the state specified by \hat{P}_2 and \hat{T}_2 . We can evaluate the entropy change for taking the ideal gas from state 1 to state 2 by a two-step path. We first compress the gas isothermally at \hat{T}_1 from \hat{P}_1 to \hat{P}_2 . We then warm the gas at constant pressure \hat{P}_2 from \hat{T}_1 to \hat{T}_2 . For the first step, $d\hat{T} = 0$, and, as before, we find

$$\Delta \hat{S}_{isothermal} = -\hat{n}R \ln \frac{\hat{P}_2}{\hat{P}_1} = \hat{n}R \ln \frac{\hat{V}_2}{\hat{V}_1}$$

For the second step, $d\hat{P} = 0$, and

$$\Delta \hat{S}_{isobaric} = \int_{\hat{T}_1}^{\hat{T}_2} \frac{\hat{n}C_P}{T} dT = \hat{n}C_P \ln \frac{\hat{T}_2}{\hat{T}_1}$$

The entropy change for the ideal-gas heat reservoir is thus

$$\Delta \hat{S} = \Delta \hat{S}_{isothermal} + \Delta \hat{S}_{isobaric} = -\hat{n}R \ln \frac{\hat{P}_2}{\hat{P}_1} + \hat{n}C_P \ln \frac{\hat{T}_2}{\hat{T}_1}$$

and we have $\Delta S = -\Delta \hat{S}$.

The essential point of the entropy-measuring machine is that we can determine the entropy change for any process without knowing anything about the process except how to control the system pressure and temperature so that the process occurs reversibly. Of course, this one reason that the entropy-measuring machine is not a practical device. To control the machine in the required manner, we must know how the thermodynamic properties of the system are related to one another on the Gibbsian manifold that defines the system's equilibrium states. If we know this, then we know $(\partial H/\partial T)_P$ and $(\partial V/\partial T)_P$ for the system along any reversible path, and we can calculate the entropy change for the system in the same way that we calculate the entropy change for the ideal-gas heat reservoir. If we have the information needed to perform the measurement, we can calculate the entropy change without using the machine.

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