

## 5 Thermal Interaction

- A. Thermal equilibrium
- B. Approach to thermal equilibrium
- C. Summary

Macroscopic systems interact most commonly in processes where heat is transferred from one system to another. The ideas developed in the preceding chapter will now be used to examine why and when such heat transfers occur. This examination will also clarify the fundamental importance of the absolute temperature.

### A. Thermal equilibrium

Consider two macroscopic systems X and X' neither of which does any macroscopic work (e.g., the volumes of these systems remain constant). The systems are, however, in contact with each other so that they can interact thermally, i.e., so that heat can be transferred from one to the other. The entire system X\*, consisting of X and X', is isolated from its surroundings. (The systems are schematically indicated in Fig. A-1. For example, a spoon X might be immersed in a cup of tea X'. Or a can of ginger ale X, previously removed from a refrigerator, might be surrounded by the air X' in a room.)

**Implications of energy conservation.** The system X has some internal energy E and the system X' has some internal energy E'. Since the entire system X\* is isolated, its total internal energy E\* must remain constant, i.e.,

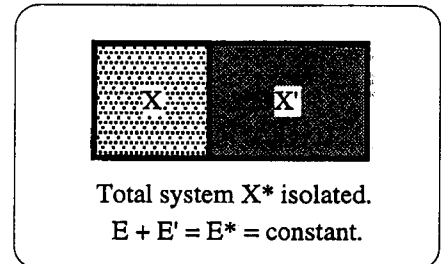
$$E + E' = E^* = \text{constant.} \quad (\text{A-1})$$

This total energy can, however, be distributed over the atoms in the two systems in many possible ways. Thus the energy E of X can have any value. Because of the conservation of energy (A-1), the energy E' must then have the corresponding value

$$E' = E^* - E. \quad (\text{A-2})$$

Any increase of the energy of X must thus be accompanied by a corresponding decrease of the energy of X'. In other words, corresponding changes  $\Delta E$  and  $\Delta E'$  of the energies of the systems are always related so that

$$\Delta E' = -\Delta E. \quad (\text{A-3})$$



**Fig. A-1.** Two thermally interacting systems X and X' (thermally insulated from their surroundings).

### Thermal equilibrium between two systems

**Probabilities of various energies.** Although X *can* have any energy E, some values of this energy are much more probable than others. To be specific, consider the situation where the entire system X\* is in equilibrium. What then is the probability P(E) that the energy of X is equal to E? As discussed in Sec. 4A, this probability is proportional to the number of basic states  $\Omega^*(E)$  that are available to the entire isolated system X\* when X has this energy E. In other words,

$$P(E) = c \Omega^*(E) \quad (\text{A-4})$$

where c is some constant. The logarithm of this probability is then simply related to the entropy S\* of the total system X\*, i.e.,

$$\ln P(E) = \ln c + \ln \Omega^*(E) = \ln c + (1/k) S^*(E). \quad (\text{A-5})$$

This merely expresses quantitatively the fact that a situation of larger entropy corresponds to a more probable situation.

But, as discussed in Sec. 4F, the entropy of the total system X\* is simply equal to the sum of the entropies of its parts X and X'. Thus

$$\ln P(E) = \ln c + (1/k) [S(E) + S'(E')] \quad (\text{A-6})$$

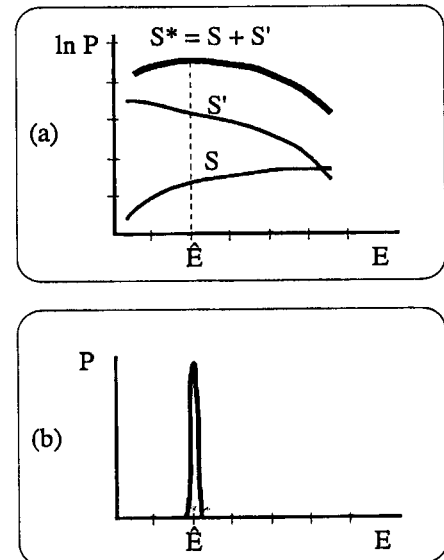
where S(E) is the entropy of X when it has an energy E and S'(E') is the entropy of X' when it has the corresponding energy E' = E\* - E.

**Dependence of probability on energy.** How then does the probability P(E) depend on the energy E? As discussed in Sec. 4F, the entropy of a system increases with its internal energy. What then happens if the energy E of X increases? The entropy of S then also increases. But the energy E' of the other system X' then decreases so that its entropy S' also decreases. As indicated in Fig. A-2a, the sum of the increasing entropy S and of the decreasing entropy S' then leads to a maximum of their sum S + S' (i.e., to a maximum of the entropy S\* of the total system). Correspondingly, ln P(E) in (A-6) exhibits a maximum at some particular value  $\hat{E}$  of the energy E.

The probability itself varies with the energy much more rapidly than the logarithm of the probability. As indicated in Fig. A-2b, a maximum of ln P(E) corresponds then to a very sharp maximum of the probability P(E) itself. Thus we arrive at the following conclusion: *When two systems X and X' are in equilibrium, the energy of each system is most likely to be very near to a most probable value* (although very small fluctuations around this value can occur).

**Most probable energy.** As the energy E changes by any small amount dE, the logarithm ln P of the probability increases or decreases by a corresponding small amount. However, it neither increases or decreases when it is at its maximum (i.e., at the very top of the smooth curve in Fig. A-2a). In other words, at the particular energy E =  $\hat{E}$  where ln P is maximum, a very small change dE of the energy produces no corresponding change of ln P.

The value of the constant c is of no great interest. It could, however, be determined since we know that the sum of the probabilities, for all possible values of the energy E, must be equal to 1.



**Fig. A-2.** Probability P that a system X has an energy E when it is in equilibrium with another system X'. (a) Logarithm of this probability, and entropies S and S' of the systems X and X'. (b) The probability P itself.

A maximum of ln P corresponds also to a maximum of P itself. Indeed, if  $d(\ln P) = 0$ , then it also true that  $dP = 0$ .

$$\text{For most probable situation,} \quad d(\ln P) = 0. \quad (\text{A-7})$$

By (A-5), this implies correspondingly that the entropy  $S^*$  of the total system does not change, i.e.,

$$\text{For most probable situation,} \quad dS^* = dS + dS' = 0. \quad (\text{A-8})$$

But a system's entropy changes with its energy in a manner specified by the absolute temperature, i.e., in the manner specified by (4F-7). Hence (A-8) can be expressed in the form

$$\frac{dE}{T} + \frac{dE'}{T'} = 0. \quad (\text{A-9})$$

But, as already mentioned in (A3), the conservation of energy for the entire system implies that  $dE' = -dE$ . Hence (A-9) implies that

$$dE \left( \frac{1}{T} - \frac{1}{T'} \right) = 0$$

so that

$$\frac{1}{T} = \frac{1}{T'}$$

or

$$\boxed{T = T'}. \quad (\text{A-10})$$

**Thermal equilibrium and temperature equality.** Thus we arrive at the following conclusion: When two systems are in thermal equilibrium, the most probable situation is one where their absolute temperatures are equal. (The most probable energies of the systems are then such that this temperature equality is true). Since this situation is overwhelmingly more probable than any other, this important conclusion can be more briefly summarized as follows:

$$\boxed{\text{When two systems are in thermal equilibrium, their absolute temperatures are equal.}} \quad (\text{A-11})$$

### Mutual equilibrium among several systems

What then are the corresponding conclusions if one is dealing with several systems, e.g., with three systems  $X$ ,  $X'$ , and  $X''$ ? Suppose that the absolute temperatures of  $X$  and  $X'$  are the same so that  $T = T'$ . Suppose that the absolute temperatures of  $X$  and  $X''$  are also the same so that  $T = T''$ . Then the following is an obvious algebraic conclusion:

$$\text{If } T = T' \text{ and } T = T'', \quad \text{then} \quad T' = T''. \quad (\text{A-12})$$

This purely mathematical conclusion has, however, the following important physical implications.

(a) Suppose that the systems  $X$  and  $X'$  are placed in contact with each other and that their absolute temperatures  $T$  and  $T'$  are already equal. Then these systems will remain in thermal equilibrium without any transfer of energy from one to the other.

(b) Similarly, suppose that the systems X and X' are placed in contact with each other and that their absolute temperatures T and T' are already equal. Then these systems will remain in thermal equilibrium without any transfer of energy from one to the other.

(c) But according to the mathematical conclusion (A-12), the absolute temperatures of X' and X'' are then also the equal. This then implies that, if the systems X' and X'' are placed in contact with each other, they too will remain in thermal equilibrium without any transfer of energy from one to the other.

Thus we arrive at the following important conclusion:

**Mutual thermal equilibrium** (*zeroth law of thermodynamics*).

If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other. (A-11)

**Application to thermometers.** The conclusion (A-11) has an immediate application to the use of thermometers. Indeed, consider any arbitrary thermometer (whose "reading" might be the height of some liquid inside a glass tube or the position of a pointer on some dial). Suppose that this thermometer indicates some particular reading when it is placed in contact with some system X and allowed to come to equilibrium with it. Suppose that it also indicates the *same* reading when it is placed in contact with some other system X' and allowed to come to equilibrium with it. Irrespective of the nature of the thermometer used, one can then immediately conclude that the systems X and X' will remain in thermal equilibrium if they are placed in contact with each other.

## Problems

### [A-1] Thermal equilibrium between two gases

A system X consists of a thin-walled box containing  $2 \times 10^{22}$  molecules of argon gas. The table in Fig. A-3 indicates how the entropy S of this system increases with its internal energy E. Another system X' consists of a thin-walled box containing  $3 \times 10^{22}$  molecules of helium gas. The table in Fig. A-3 also indicates how the entropy S' of this system increases with its internal energy E'. When these two systems are initially separated, the internal energy  $E_i$  of X (the box of argon) is 140 J and the internal energy  $E_i'$  of X' (the box of helium) is 160 J. The two systems are now brought into contact so that energy (in the form of heat) can be transferred from one to the other.

- Complete the table in Fig. A-4 by listing, for each of the indicated values of the energy E of the system X, the corresponding values of the energy E' and entropy S' of the system X'. Also list the values of the total entropy S\* of the entire system consisting of both systems.
- At what energy E does the total entropy S\* attain its maximum value?
- After the two systems have come into thermal equilibrium with each other, what is the most probable energy  $\hat{E}$  of X (the box of argon)? What is the most probable energy  $\hat{E}'$  of X' (the box of helium)?
- Suppose that the entire energy of both gases is distributed over the gas molecules in such a way that every gas molecule (whether argon or helium) has the *same* energy. What then would be the energy of each molecule? What would be the energy of the argon gas? What would be the energy of the helium gas? Are these energies the same as the most probable energies calculated in part c? <a-3>

E (joule)	S ( $10^{22}$ k)	E' (joule)	S' ( $10^{22}$ k)
60	12.3	60	18.4
80	13.1	80	19.7
100	13.8	100	20.7
120	14.4	120	21.5
140	14.8	140	22.2
160	15.2	160	22.8
180	15.6	180	23.4
200	15.9	200	23.8
220	16.2	220	24.3
240	16.4	240	24.7

Fig. A-3. Tables indicating how the entropies of the two systems X and X' in Problem A-1 increase with their internal energies. (The entropy is expressed as a multiple of the quantity  $10^{22}$  k where k is Boltzmann's constant.)

E (joule)	S ( $10^{22}$ k)	E' (joule)	S' ( $10^{22}$ k)	S* ( $10^{22}$ k)
60	12.3			
80	13.1			
100	13.8			
120	14.4			
140	14.8			
160	15.2			
180	15.6			
200	15.9			
220	16.2			
240	16.4			

Fig. A-4. Table listing the corresponding energies and entropies of the systems X and X' described in Problem A-1.

**[A-2] Check of temperature equality**

In equilibrium, the absolute temperatures of the two systems in the preceding problem should be equal. But  $dS/dE = 1/T$  or  $dS = dE/T$ . The same small energy change of X or X' should, therefore, produce the same entropy change in each of the two systems.

The following questions ask you to check this conclusion *approximately* by using the table in Fig. A-3. (This table provides information about energy changes of 20 J which are large enough to be only approximately small).

- How much does the entropy of X (the box of argon) increase when its energy is increased by 20 J above its most probable value in equilibrium?
- How much does the entropy of X' (the box of helium) increase when its energy is increased by 20 J above its most probable value in equilibrium?
- Are these entropy increases approximately equal?  $\langle a-b \rangle$

**B. Approach to thermal equilibrium**

The preceding section discussed two systems X and X' in thermal contact so that energy (in the form of heat) can be transferred from one to the other. When the systems are in equilibrium, the overwhelmingly most probable situation is then the one where the absolute temperature of the systems are equal.

What happens if the absolute temperatures of the two systems are initially *not* equal and the systems are then brought into thermal contact so that energy can be transferred from one to the other? The entire isolated system X\*, consisting of X and X', is then in a situation far from its most probable one. Hence the situation will change until the most probable equilibrium situation is reached.

Let us then look in greater detail at the process occurring during the approach to equilibrium.

**Initial non-equilibrium situation.** Before the systems are brought into thermal contact, and immediately afterwards, they have different initial absolute temperatures  $T_i$  and  $T_i'$ . Thus

$$T_i \neq T_i'. \quad (\text{B-1})$$

This is then not an equilibrium situation. Thus X has an energy E different from its most probable energy  $\hat{E}$  in equilibrium. The initial energies  $E_i$  and  $E_i'$  of the systems differ then from their most probable equilibrium values, i.e.,

$$E_i \neq \hat{E} \quad \text{and} \quad E_i' \neq E^* - \hat{E}. \quad (\text{B-2})$$

**Final equilibrium situation.** When the systems have attained their final equilibrium situation, their final absolute temperatures  $T_f$  and  $T_f'$  are equal. Thus

$$T_f = T_f'. \quad (\text{B-3})$$

Furthermore, the final energies  $E_f$  and  $E_f'$  of the systems are extremely close to their most probable values. Thus

$$E_f = \hat{E} \quad \text{and} \quad E_f' = E^* - \hat{E}. \quad (\text{B-4})$$

**Energy changes.** During the approach to equilibrium, the energy  $E^*$  of the entire isolated system remains unchanged, i.e.,

$$\Delta E^* = 0. \quad (\text{B-5})$$

However, the energy of each system changes because heat is transferred from one system to the other. Because of the constancy (B-5) of the total energy, the energy change  $\Delta E$  and  $\Delta E'$  of the systems are related so that

$$\Delta E + \Delta E' = 0 \quad (\text{B-6})$$

or 
$$Q + Q' = 0. \quad (\text{B-7})$$

where the heats  $Q$  and  $Q'$  absorbed by the two systems are equal to

$$Q = \Delta E = E_f - E_i, \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} (\text{B-8})$$

and 
$$Q' = \Delta E' = E_f' - E_i'.$$

**Entropy changes.** Since the entire system approaches the most probable situation where its final entropy is maximum, this final entropy  $S_f^*$  is larger than its initial entropy  $S_i^*$ . Thus

$$S_f^* > S_i^*. \quad (\text{B-9})$$

During the process of approaching equilibrium, the entropy of the system thus increases (i.e., it changes by a positive amount  $\Delta S^* = S_f^* - S_i^*$ ). Thus

$$\Delta S^* = \Delta S + \Delta S' > 0. \quad (\text{B-10})$$

**Colder and warmer systems.** The relation (B-7) between the absorbed heats implies that the heats  $Q$  and  $Q'$  absorbed by the two systems have opposite signs. i.e.,

$$Q = -Q'. \quad (\text{B-11})$$

When one of the systems absorbs positive heat (so that its internal energy increases), the other system then absorbs negative heat (so that its internal energy decreases). The words *colder* and *warmer* are conventionally used to distinguish between these two systems.

Def: **Colder system:** The system which absorbs positive heat when thermally interacting with some other system. (B-12)

Def: **Warmer system:** The system which absorbs negative heat (i.e., which gives off positive heat) when thermally interacting with some other system. (B-13)

**Heat flow and absolute temperatures.** As discussed in Sec. 4F, the absolute temperature of any ordinary macroscopic system is positive and increases with its internal energy. Thus one reaches the following conclusions:

If the system X absorbs positive heat, so that its energy increases, then its absolute temperature correspondingly increases. The other system Y then absorbs negative heat so that its energy decreases; hence its absolute temperature correspondingly decreases. Hence the final common absolute temperature  $T_f$ , attained by the systems when they have reached equilibrium, has a value somewhere between the initial temperatures of these systems, i.e.,

$$T_i < T_f < T_i' . \quad (\text{B-14})$$

The preceding comments also indicate the following: The system which has initially the lower absolute temperature is the one which absorbs positive heat (i.e., it is the colder system). The system which has initially the higher absolute temperature is the one which absorbs negative heat (i.e., which gives off positive heat and is thus the warmer system). Hence there exists the following connection between absolute temperatures and the direction of heat flow:

Heat flows from the system at the higher absolute temperature to the system at the lower absolute temperature. (B-15)

Equivalently, this means that the system at the higher absolute temperature is the warmer system (i.e., the system which give off positive heat) and the system at the lower absolute temperature is the colder system (i.e., the system which absorbs positive heat).

## Problems

### [B-1] Approach to equilibrium of two gases

Refer back to Problem A-1 which discussed two systems X and X' which were initially separated and then brought into thermal contact. (The system X was a box containing  $2 \times 10^{22}$  molecules of argon gas with an initial energy of 140 J. The system X' was a box containing  $3 \times 10^{22}$  molecules of helium gas with an initial energy of 160 J)

- (a) In the process of reaching thermal equilibrium, how much heat was absorbed by the system X? How much heat was absorbed by the system X'? What was the change  $\Delta E^*$  of the internal energy of the entire system consisting of X and X'?
- (b) Which of the two systems had initially the larger internal energy? Which of them had initially the larger absolute temperature? <h-4>
- (c) In the process of reaching thermal equilibrium, what was the change  $\Delta S$  of the entropy of X? What was the change  $\Delta S'$  of the entropy of X'? What was the change  $\Delta S^*$  of the entropy of the entire system consisting of X and X'? <a-1>

### [B-2] Can thermometers indicate non-equilibrium?

A thermometer in equilibrium with a system X indicates a different reading than when it is in equilibrium with another system Y. If the systems X and Y are now placed into thermal contact with each other, will they be in thermal equilibrium or will heat be transferred from one to the other? Explain the reasoning leading to your conclusion. <h-2> <a-8>

### [B-3] Information provided by an arbitrary thermometer

Consider any arbitrary thermometer (e.g., one consisting of a thin glass tube filled with a liquid like water or alcohol). The reading of the thermometer might

then be the number indicated by a pointer on some dial (or the length of the column of liquid in the preceding glass tube).

Suppose that the reading of the thermometer is larger when it is placed in contact with system X than when it is in contact with system Y. Answer the following questions if this is possible. Otherwise, state that the information is inadequate to reach a definite conclusion (e.g., that it may depend on the nature of the thermometer or the nature of the liquid in the glass tube).

- (a) Will the systems X and Y be in equilibrium when placed in contact with each other?
- (b) Will heat flow from X to Y (so that Y absorbs positive heat) or will heat flow from Y to X (so that X absorbs positive heat)?
- (c) Which of the two systems has the larger absolute temperature?
- (d) Can this thermometer be used to determine the absolute temperatures of X and of Y? <a-5>

**[B-4] *Thermometer indicating absolute temperature***

Imagine that somebody is clever enough to construct a special thermometer whose dial reading indicates the absolute temperature of the thermometer itself. Suppose the reading of this thermometer is again larger when it is placed in contact with system X than when it is placed in contact with system Y.

Answer for this thermometer the same questions as those in the preceding problem. <a-2>

## C. Summary

### Definitions

**Colder system:** The system which absorbs positive heat when thermally interacting with some other system.

**Warmer system:** The system which absorbs negative heat (i.e., which gives off positive heat) when thermally interacting with some other system.

### Important knowledge

**Temperature equality in thermal equilibrium:** When two systems are in thermal equilibrium, their absolute temperatures are equal.

**Mutual thermal equilibrium (zeroth law of thermodynamics):** If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other.

**Approach to thermal equilibrium:**

- \* Total energy remains constant. Total entropy increases (as the entire system approaches a more probable situation).
- \* Heat flows from the system at the higher absolute temperature to the system at the lower absolute temperature.

### New abilities

You should now be able to do the following:

- (1) Use the temperatures indicated by thermometers to decide whether systems will be in equilibrium when placed into thermal contact with each other.
- (2) Knowing the absolute temperatures of two systems, determine which of the systems (if any) will absorb or give off positive heat.



## Problems

### [C-1]† Probabilities in thermal equilibrium

When two systems X and X' are in thermal equilibrium, the entropy  $S^*$  of the entire isolated system (consisting of X and Y) depends on the energy E of X. Suppose that this entropy has a value  $S_1^*$  when the energy is  $E_1$ , and that it has a value  $S_2^*$  when the energy is  $E_2$ .

- What then is the ratio  $P_1/P_2$  of the probability  $P_1$  that X has an energy  $E_1$  compared to the probability  $P_2$  that it has an energy  $E_2$ ? (Express your answer in terms of the entropies.)
- Problem A-1 dealt with two gases X and X' which were in mutual equilibrium after being initially separate. In this equilibrium situation, what is the approximate value of the ratio  $P_1/P_2$  where  $P_1$  is the probability that X has its most probable energy of 120 J and  $P_2$  is the probability that X still has the energy of 140 J which it had initially? <h-1> <a-10>

### [C-§]‡ Spin systems and negative absolute temperature

The nuclei of some atoms (like hydrogen atoms) are characterized by a property called "spin". Hence they behave like small bar magnets which can be aligned either along, or opposite to, the direction of an applied magnetic field. (The energy of such a little magnet is smallest when it is aligned along the field and largest when it is aligned opposite to it.) In some special situations these spins can be considered separately (while ignoring the kinetic energies of the nuclei) because there is negligible transfer of magnetic energy into kinetic energy.

Consider a system consisting of N such spin magnets. (a) There is only one way that all these magnets can be lined up so that all of them point along the magnetic field. The entropy of the system of spins is then zero (since  $\ln\Omega = 0$  if  $\Omega = 1$ ). Furthermore, the energy of the system has then its smallest possible value. (b) Similarly, there is only one way that all these magnets can be lined up so that all of them point opposite to the magnetic field. The entropy of the system of spins is then again zero. Furthermore, the energy of the system has then its largest possible value. (c) However, there are many ways that the magnets can be lined up so that some of them are pointing along the field and some of them opposite to it. Correspondingly, the entropy of the system is quite large at energies between the preceding two extreme situations.

The entropy  $S$  of the system thus varies with its energy in the manner indicated in Fig. C-1.

- The basic temperature  $\beta$  of a system is defined as the rate of change of its basic entropy with energy, [i.e.,  $\beta = d(\ln\Omega/dE)$ ]. Thus  $\beta$  is the slope of the curve in the graph of Fig. C-1. Consider this basic temperature at the energies  $E_1, E_2, E_3, E_4,$  and  $E_5$  (where  $E_3$  is the energy where the entropy is maximum).
  - At each of these energies, is the basic temperature of the spin system positive, negative, zero, or infinitely large.
  - As the energy of the system increases, does its basic temperature increase or decrease?
  - When the system gives off positive heat (i.e., absorbs negative heat) does its basic temperature increase or decrease? Does a warmer system (i.e., one which gives off positive heat) then have a larger or smaller basic temperature than a colder system? <a-7>
- By its definition, the absolute temperature  $T$  is related to the basic temperature so that  $kT = 1/\beta$ .
  - At each of the energies  $E_1, E_2, E_3, E_4,$  and  $E_5$  is the absolute temperature of the spin system positive, negative, zero, or infinitely large?

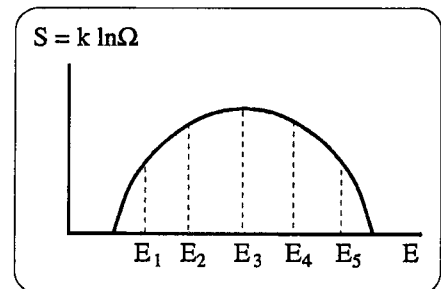


Fig. C-1. Graph showing how the entropy of a spin system varies with its energy.

(2) As the energy of the system increases from  $E_1$  to  $E_2$ , does its absolute temperature  $T$  increase or decrease? As the energy of the system increases from  $E_4$  to  $E_5$ , does its absolute temperature  $T$  increase or decrease?

(3) Suppose that the system gives off positive heat so that its energy decreases from  $E_4$  to  $E_2$ . Is the system's initial absolute temperature then positive or negative? Is its final absolute temperature positive or negative? When giving off this heat, does the system's absolute temperature then increase or decrease?

(4) Is a system which has a negative absolute temperature warmer or colder than one which has a positive absolute temperature? <a-4>