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Reversible and Irreversible Heating and Cooling

When one writes $\Delta S \geq q/T$, what differentiates the circumstances in which the equality applies from those governed by the inequality? The standard answer is that the equality applies only to changes conducted reversibly, and the inequality to all other changes. Quite apart from the notorious difficulties that beginners find in the concept of reversibility, the standard answer is far from satisfactory: we do, after all, apply the equality to a great many highly irreversible changes. For a liquid in vigorous ebullition under atmospheric pressure, we calculate ΔS_{vap} as $\Delta H_{vap}/T_{bp}$; when a system undergoes some irreversible alteration, we still calculate the resultant entropy change in the surroundings as $\Delta S_{surr} = -q_{syst}/T_{surr}$; and so on in numerous other instances. To be sure, such procedures are supported by excellent justifications, but the justifications are not always clear to students who may, in consequence, come to the disastrous conclusion that the two cases comprised in the expression $\Delta S \geq q/T$ are differentiated only by some subtle *qualitative* distinction. Giving rise to much of the mystique commonly associated with q_{rev}, this conclusion is disastrous also because it directs attention away from the completely unmysterious *quantitative* distinctions that differentiate the two cases.

In very essence a quantitative concept, the idea of reversibility derives its meaningfulness solely from the systematic extrapolation that links an ideal limit with events of the real world. This view of reversibility is brilliantly highlighted in two simple lecture experiments described by Eberhardt.[1,2] Through measurements of mechanical and electrical work, respectively, these experiments demonstrate the progressive approach of work inputs and outputs toward a common limiting magnitude (w_{rev}) which, though it refers to a wholly unrealizable ideal experiment, is nevertheless a quantity fully established by way of real experiments. In these cases one thus shows that, when the given change proceeds along the given path, $w_{rev} \geq w$; and, with ΔE a constant for the given change, it then follows necessarily that $q_{rev} \geq q$. This is the first and most obvious quantitative difference between the circumstances referred to by the bimodal relation $\Delta S \geq q/T$. For if by definition $\Delta S \equiv q_{rev}/T$ then, in any circumstances where $q_{rev} > q$, clearly $\Delta S > q/T$.

The second quantitative difference, scarcely less obvious but usually much less emphasized, arises whenever the operative circumstances ensure that the quantity of work performed shall be independent of the degree to which the specified change is conducted reversibly or irreversibly. In such circumstances q can be equated to q_{rev}, but of course the reversible and irreversible changes remain associated with quite different values of ΔS. Though the q's are equal, the values of ΔS still reflect quantitative differences in the temperatures of any heat sources or sinks involved. Precisely how the variation in ΔS arises from these temperature differences is illustrated in the following analysis of a very simple specific case: the cooling (or warming) of an object in a manner that is, to any desired degree, reversible or irreversible. This analysis is conceived as demonstrating for transfers of heat just what Eberhardt's experiments demonstrate for work transfers.

Cooling in Geometric Series

By successive contact with some number (n) of large heat reservoirs or baths, let an object be cooled from some initial temperature T_i to some final temperature T_f. Over the temperature range T_i to T_f, let the object have an effectively invariant heat capacity of C cal/g—representing either C_P or C_V, according to the conditions of the experiment. Whether the cooling is conducted reversibly or irreversibly, with entropy established as a function of state we know that the entropy change (ΔS_J) of the object will remain constant at

$$\Delta S_J = C \ln (T_f/T_i) = -C \ln (T_i/T_f) \qquad (1)$$

What is the corresponding entropy change (ΔS_B) in the n large baths used to cool the object from T_i to T_f? Let the baths be numbered in order of temperatures *decreasing* from T_i: namely, in the order T_i,

[1] Eberhardt, W. H., J. Chem. Educ., **41**, 483 (1964).
[2] Eberhardt, W. H., J. Chem. Educ., **47**, 362 (1970).

$T_1, T_2, \ldots T_n$, where T_n represents the temperature (T_f) of the last bath used in cooling the object. And let us now suppose that the temperatures of the successive baths descend in a geometric series. That is, let the temperature of each bath represent a constant fraction of the temperature of the object as it comes to that bath. Then

$$T_1 = \frac{1}{\alpha} T_i; \; T_2 = \frac{1}{\alpha} T_1; \; \ldots$$

or

$$T_i/T_1 = T_1/T_2 = \ldots = \alpha$$

Thus

$$T_i/T_2 = \alpha^2$$

and

$$T_i/T_f = T_i/T_n = \alpha^n \tag{2}$$

Each bath at temperature T_y receives the heat discharged by the object as it is cooled from the temperature T_x of the preceding bath, so that $\Delta S_y = C(T_x - T_y)/T_y$. The aggregate entropy change (ΔS_B) for the entire set of n baths is then

$$\Delta S_B = \Sigma q/T = \frac{C(T_i - T_1)}{T_1} + \frac{C(T_1 - T_2)}{T_2} + \ldots + \frac{C(T_{n-1} - T_n)}{T_n}$$

$$= C\left[\frac{T_i - T_i/\alpha^1}{T_i/\alpha^1} + \frac{T_i/\alpha^1 - T_i/\alpha^2}{T_i/\alpha^2} + \ldots + \frac{T_i/\alpha^{n-1} - T_i/\alpha^n}{T_i/\alpha^n}\right]$$

$$= C[(\alpha - 1) + (\alpha - 1) + \ldots + (\alpha - 1)]$$

Since the summation evidently comprises n identical terms, it follows that

$$\Delta S_B = nC(\alpha - 1) \tag{3}$$

Equation (2) at once permits us to express α in terms of the particular T_i and T_f specified in the problem at issue, and the last equation can then be rewritten with n as the only free variable

$$\Delta S_B = nC([T_i/T_f]^{1/n} - 1) \tag{4}$$

This equation permits a very simple computation of ΔS_B as a function of the number of baths employed.

How shall we evaluate the total entropy change ($\Delta S_B{}^*$) when the number of baths $n \rightarrow \infty$? Rearrangement of eqn. (4) yields for this limiting case

$$\left(1 + \frac{\Delta S_B{}^*}{nC}\right) = [T_i/T_f]^{1/n}$$

or

$$\lim_{n\rightarrow\infty}\left[1 + \frac{1}{nC/\Delta S_B{}^*}\right]^n = T_i/T_f$$

A change of variable is now affected by defining $\gamma \equiv nC/\Delta S_B{}^*$. This entails that $\gamma \rightarrow \infty$ as $n \rightarrow \infty$, and we can express n in terms of γ, as $n = \gamma\Delta S_B{}^*/C$. Substituting in the last equation above, we find

$$\lim_{\gamma\rightarrow\infty}\left[\left(1 + \frac{1}{\gamma}\right)^\gamma\right]^{\Delta S_B{}^*/C} = T_i/T_f$$

But in the limit $\gamma \rightarrow \infty$ we well know that the function $(1 + 1/\gamma)^\gamma \rightarrow e$, where e symbolizes the base of natural logarithms, 2.718 . . . . Consequently

$$e^{\Delta S_B{}^*/C} = T_i/T_f$$

and

$$\Delta S_B{}^* = C \ln (T_i/T_f) \tag{5}$$

Comparing this finding with eqn. (1), we see that, in the limit of a number of baths $n \rightarrow \infty$, the aggregate entropy increase of the baths perfectly matches the entropy decrease of the object cooled! And in this limit alone we encounter the truly reversible cooling for which we can write as the net effect

$$\Delta S_{tot} = \Delta S_{syst} + \Delta S_{surr} = \Delta S_J + \Delta S_B{}^* = 0$$

Heating in Geometric Series

When an object with heat capacity C is heated from some initial temperature T_i to a higher final temperature T_f, we have as before

$$\Delta S_J = -C \ln (T_i/T_f)$$

Here, with $T_i < T_f$, $-C \ln (T_i/T_f)$ represents a positive quantity (rather than the corresponding negative quantity found in a cooling experiment). Let the object be warmed from T_i to T_f by a series of baths we now number in order of *increasing* temperatures, as $T_i, T_1, T_2, \ldots T_n$, where T_n now represents the temperature (T_f) of the last bath used in warming the object. Again supposing that the temperatures of the successive baths constitute a geometric series, we find exactly as before that

$$T_i/T_f = T_i/T_n = \alpha^n$$

The only difference is that in the cooling experiment, with $T_i > T_f$, we have $\alpha > 1$; while in the present heating experiment, with $T_i < T_f$, we have $\alpha < 1$. The rest of the analysis of the heating operation is also formally identical with that earlier made for the cooling operation. In the heating experiment each bath at temperature T_y gives up to the object the heat required to warm it from the lower temperature T_x of the preceding bath. The earlier relation, $\Delta S_y = C(T_x - T_y)/T_y$ then remains perfectly correct, since $(T_x - T_y)$ is now a negative quantity properly corresponding to the necessarily negative value of ΔS_y. Thus the analysis proceeds unchanged, and again yields eqn. (4). With $T_i < T_f$, the right side of the equation yields for ΔS_B an appropriately negative value. And the limiting negative value assumed by ΔS_B will be calculable as before from eqn. (5).

Heating and Cooling in Arithmetic Series[3]

We turn now to brief consideration of how an object will be cooled by successive immersion in a series of n baths with temperatures equally spaced between the extremes of T_i and T_f, i.e., bath temperatures that constitute an arithmetic series with spacing equal to $(T_i - T_f)/n$. Each bath at temperature T_y then receives the heat discharged by the object as it is cooled from the temperature (T_x) of the preceding bath. Therefore

[3] See DUGDALE, J. S., "Entropy and Low-Temperature Physics," Hutchinson, London, **1966**, pp. 66–67; or NASH, L. K., "Elements of Chemical Thermodynamics," (2nd ed.), Addison-Wesley, Reading, Mass., **1970**, p. 168.

$$\Delta S_y = \frac{C(T_i - T_f)/n}{T_y}$$

and the numerator will clearly be the same for all baths in the series. The aggregate entropy change (ΔS_b) for the entire set of n baths is then

$$\Delta S_b = \frac{C(T_i - T_f)/n}{T_i - [(T_i - T_f)/n]} + \frac{C(T_i - T_f)/n}{T_i - [2(T_i - T_f)/n]} + \ldots + \frac{C(T_i - T_f)/n}{T_i - n[(T_i - T_f)/n]}$$

where the denominator of the last term duly reduces to T_f, as it should. The indicated summation can now be formulated more compactly in terms of an index number j, which is all that differentiates any term from those that precede and follow it.

$$\Delta S_b = \sum_{j=1}^{j=n} \frac{C(T_i - T_f)}{nT_i - j(T_i - T_f)} = C \sum_{j=1}^{j=n} \frac{1}{[nT_i/(T_i - T_f)] - j} \quad (6)$$

From this summation we can calculate ΔS_b for small numbers of baths, and when the number of baths $n \rightarrow \infty$ we can estimate the limiting aggregate entropy change of the baths (ΔS_b^*) by the following argument[4]

$$\frac{\Delta S_b^*}{C} = \lim_{n\to\infty} \sum_{j=1}^{j=n} \frac{1}{[(nT_i)/(T_i - T_f)] - j}$$

$$= \lim_{n\to\infty} \int_1^n \frac{dj}{[(nT_i)/(T_i - T_f)] - j}$$

$$= \lim_{n\to\infty} \ln\left[\frac{T_i}{T_f} - \frac{(T_i - T_f)}{nT_f}\right] = \ln \frac{T_i}{T_f} \quad (7)$$

As before, when the object is *heated* by baths with temperatures that *ascend* in arithmetic series, the resultant expressions remain formally identical with those just found for the corresponding cooling operation. And in either case the limit established by eqn. (7) remains identical with that established for baths with temperatures that stand in geometric series.

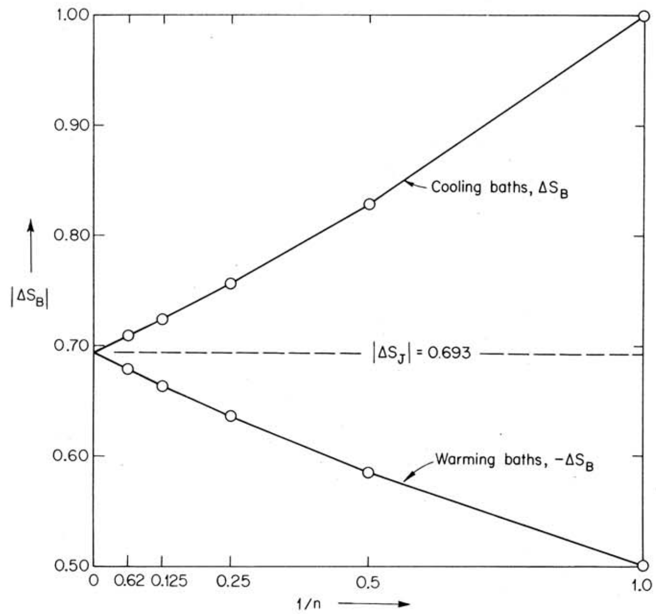
A Sample Calculation

Throughout the foregoing entropy evaluations, the heat capacity (C) enters only as a constant multiplier in all the functions involved. Interest thus centers on the *other* parts of those functions and, in our example, C will be altogether suppressed—simply by setting it equal to 1. And for this example let us take $T_i/T_f = 2$ in the cooling experiment and $T_i/T_f = {}^1/_2$ in the warming experiment.

For the object, in warming and cooling, respectively

$$\Delta S_J = -C \ln (T_i/T_f) = \pm \ln 2 = \pm 0.693$$

The aggregate entropy change of the baths is then as shown in the accompanying table for sets of baths in which $n = 1, 2, 4, 8,$ or 16. Reading outward from the central column, which indicates the number of baths involved, we find immediately to the left the corresponding value of ΔS_B calculated from eqn. (4), and immediately to the right the value of ΔS_b calculated from eqn. (6). In the outermost columns appears the net entropy change (ΔS_{tot}) in each cooling or heating operation—calculated on the left as $\Delta S_B + \Delta S_J$, and on the right as $\Delta S_b + \Delta S_J$. Observe how very little the values of ΔS_{tot} are affected by whether the bath temperatures stand in geometric or arithmetic progression. But incomparably the most important aspect of the ΔS_{tot} values is their obvious convergence toward zero as $n \rightarrow \infty$. That is, as n increases without limit, $\Delta S_B + \Delta S_J \rightarrow 0$, so that $\Delta S_B \rightarrow -\Delta S_J$. The figure displays the surprising rapidity of this convergence.



Plot of ΔS_b versus $1/n$.

Like the analogous graphs presented by Eberhardt, this figure illustrates the progressive approach of results calculated for feasible experiments, with finite n, to the limiting value characteristic of an unattainable reversible operation with $n \rightarrow \infty$. The hypothetical ideal operation in which $\Delta S = q/T$ is thus seen to emerge as a limit fully definable in terms of results calculable for actual operations in which $\Delta S > q/T$. No more vivid illumination of the relation of the two cases joined in the expression $\Delta S \geq q/T$ is readily imaginable. Moreover, though logically equivalent, the result here obtained is psychologically quite different from that stressed in a very recent paper by Pyun.[5] To say that a transfer of heat can proceed with $\Delta S_{tot} = 0$ only when the two bodies involved stand at the very same temperature, which is Pyun's conclusion, is to leave one wondering how any strictly reversible (isentropic) cooling or heating could possibly be brought about, or even imagined. This doubt simply does not arise from the present analysis—which concludes that any amount of strictly reversible cooling or heating would be readily achievable in the limit where the number of baths $n \rightarrow \infty$. And a significantly close approach to this limit can be found in actual practice, e.g., in the operation of Stirling-cycle refrigerators.[6]

A Closed Cycle

To complete the analysis, we now examine a closed cycle of changes. By use of n baths, let an object

[4] In a much more elegant but rather lengthier analysis suggested to me by Attila Szabo, the same limit is derived by first showing that the desired summation can be equated to $\partial/\partial\beta\{\ln[(\beta - 1)!/(\beta - 1 - n)!]\}$, where $\beta = nT_i/(T_i - T_f)$. Since as thus defined β must become very large as n increases without limit, Stirling's approximation can then be brought to bear in evaluating the limiting value of the derivative, which is simply $\ln(T_i/T_f)$.

[5] PYUN, C. W., J. CHEM. EDUC., 46, 677 (1969).

Calculated Aggregate Entropy Change for Various Series of Baths

Geometric Series ΔS_{tot}	Geometric Series $\Delta S_B = n([T_i/T_f]^{1/n} - 1)$	Number of baths, n	Arithmetic Series $\Delta S_b = \sum_1^n \frac{1}{[nT_i/(T_i - T_f)] - 1}$	Arithmetic Series ΔS_{tot}
	Cooling:	$T_i/T_f = 2$ yields $\Delta S_j = -0.693$		
0.307	$1(2 - 1) = 1.000$	1	$\left(\frac{1}{1(2) - 1}\right) = 1.000$	0.307
0.135	$2(1.414 - 1) = 0.828$	2	$\left(\frac{1}{3} + \frac{1}{2}\right) = 0.833$	0.140
0.063	$4(1.189 - 1) = 0.756$	4	$\left(\frac{1}{7} + \frac{1}{6} + \ldots + \frac{1}{4}\right) = 0.760$	0.067
0.031	$8(1.0905 - 1) = 0.724$	8	$\left(\frac{1}{15} + \frac{1}{14} + \ldots + \frac{1}{8}\right) = 0.725$	0.032
0.016	$16(1.0443 - 1) = 0.709$	16	$\left(\frac{1}{31} + \frac{1}{30} + \ldots + \frac{1}{16}\right) = 0.709$	0.016
	Warming:	$T_i/T_f = 1/2$ yields $\Delta S_J = 0.693$		
0.193	$1\left(\frac{1}{2} - 1\right) = -0.500$	1	$-\left(\frac{1}{2}\right) = -0.500$	0.193
0.107	$2\left(\frac{1}{1.414} - 1\right) = -0.586$	2	$-\left(\frac{1}{3} + \frac{1}{4}\right) = -0.583$	0.110
0.057	$4\left(\frac{1}{1.189} - 1\right) = -0.636$	4	$-\left(\frac{1}{5} + \frac{1}{6} + \frac{1}{7} + \frac{1}{8}\right) = -0.635$	0.058
0.029	$8\left(\frac{1}{1.0905} - 1\right) = -0.664$	8	$-\left(\frac{1}{9} + \frac{1}{10} + \ldots + \frac{1}{16}\right) = -0.663$	0.030
0.014	$16\left(\frac{1}{1.0443} - 1\right) = -0.679$	16	$-\left(\frac{1}{17} + \frac{1}{18} + \ldots + \frac{1}{32}\right) = -0.678$	0.015

(with heat capacity $C = 1$) be cooled from some original temperature T_0 to the temperature $T_0/2$, and let the object then be rewarmed by n baths to the original temperature T_0. When $n \to \infty$, the perfectly reversible circumnavigation of this closed cycle will be completed with $\Delta S = 0$ for system and surroundings both individually and collectively. How does the situation differ when the cycle is traversed irreversibly with, say, $n = 8$ throughout? The object is itself surely returned to precisely its original state; but a glance at the table indicates, as the overall net entropy change, $\Delta S_{tot} = 0.031 + 0.029 = 0.060$ when the bath temperatures stand in geometric progression, and $\Delta S_{tot} = 0.032 + 0.030 = 0.062$ when they form an arithmetic progression. What are the specific alterations reflected in these entropy changes?

When the bath temperatures form a geometric series, the analysis is perfectly straightforward but not notably illuminating. For, save in the limit $n \to \infty$, *all* the baths used in cooling and warming the object will stand at the end in states different from those they possessed at the outset. The overall entropy change for the closed cycle then represents the sum of contributions made by all the diffuse multitude of individual changes.

When the bath temperatures form an arithmetic progression, the analysis is even simpler, and far more illuminating. For in this case the residual effects of the closed cycle are sharply localized. Save in two instances, the quantity of heat delivered to each of the n baths used in cooling the object is precisely equal to the quantity of heat subsequently drawn from each of the n baths used to rewarm the object to its original temperature. Hence all but the two exceptional baths will stand at the end in the very same states that characterized them at the outset. The net increase of entropy for the entire closed cycle must then arise solely from changes in just those two exceptional baths. The two in question are: (1) the last bath used in cooling the object to its lowest temperature $T_0/2$, for from this bath *no* heat is subsequently withdrawn when the object is rewarmed to its original temperature; and (2) the last bath used in rewarming the object to its highest temperature T_0, for to this bath *no* heat was earlier delivered in the course of the cooling operation.

From the easily evaluable alterations in these two "end" baths, the net entropy change in the closed cycle can at once be determined. If n baths are used in the initial cooling operation, the heat released to each such bath is $(T_0 - T_0/2)/n = +T_0/2n$. The entropy change (ΔS_c) of the last cooling bath, at temperature $T_0/2$, is then expressible as

$$\Delta S_c = \frac{T_0/2n}{T_0/2} = \frac{1}{n}$$

Similarly, if n baths are used in the subsequent rewarming operation, the heat drawn from each such bath is $(T_0/2 - T_0)/n = -T_0/2n$. The entropy change (ΔS_h) of the last heating bath, at temperature T_0, is then

$$\Delta S_h = \frac{-T_0/2n}{T_0} = \frac{-1}{2n}$$

For the two "end" baths together, the entropy change is thus

$$\Delta S_{tot} = \frac{1}{n} - \frac{1}{2n} = +\frac{1}{2n}$$

With, say $n = 8$ baths, this equation yields $\Delta S_{tot} = 0.062$, which is exactly the value earlier obtained from the entries in the table. *That* $\Delta S_{tot} = 1/2n$ must approach zero in the limit of $n \to \infty$ is mathematically

[6] Everett, D. H., "Chemical Thermodynamics," John Wiley & Sons, Inc., New York, **1959**, Appendix B; Kohler, J. W. L., *Sci. American*, **212**, 119 (April 1965).

perfectly evident. *Why* zero must be the limit is now intuitively perhaps even more evident—since the over-all entropy increase has been shown to represent nothing but "end-effects" which must, as always, be reduced to insignificance when a linear sequence is indefinitely prolonged.