Chem. Educator **2002,** *7,* 127–131

Carnot Cycle Revisited

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Received January 14, 2002. Accepted March 15, 2002

Abstract: Sadi Carnot stated that the efficiency of a reversible Carnot cycle is independent of the properties of the material used to run the cycle. Using this statement, all textbook discussions of the Carnot cycle use an ideal gas. Here, in contrast, we consider, in the spirit of the Caratheodory approach, a general analysis centered on the existence of an integrating factor that transforms an inexact differential into an exact differential. Also we derive a general relation between temperature and volume along an adiabatic path. Using these two results, we obtain the efficiency of the Carnot cycle, $\eta = 1 - T_C/T_H$, for any equation of state.

Introduction

In his only publication in 1824, “Réflexions sur la Puissance Motrice du Feu, et sur les Machines Propres à Développer cette Puissance” [1], Nicolas-Léonard-Sadi Carnot presented a general analysis of heat engines. In his paper, Carnot stated that the maximum amount of work is obtained by using any reversible cyclic engine, and that the maximum efficiency is independent of the material properties of the engine. Although Carnot did not translate his ideas into a mathematical language, his analysis was relevant in the development of the fundamental ideas that resulted in the postulation of the Second Law of Thermodynamics. Ten years after Carnot’s work was published, Emile Clapeyron published, in his only scientific paper, the mathematical representation of Carnot’s ideas [2, 3].

In this paper we revisit the reversible Carnot cycle and present an alternative derivation of the efficiency. Our analysis is independent of any particular relation associated with an equation of state. In the traditional pedagogy, most textbooks in their discussion of the Carnot cycle use the ideal-gas equation [3–8]. Using relations among variables only satisfied by the ideal gas, authors calculate the efficiency of the cycle. Now using Carnot’s ideas, the result obtained using the ideal gas, in principle, can be extrapolated to any equation of state describing the material properties of a gas. This result also suggests the existence of an exact differential. This approach leaves some students wondering and needing to believe Carnot’s statement. Thus, a derivation that relies on a general thermodynamic relation satisfied by any equation of state gives students a better grasp of Carnot’s statement on the material properties independence.

Although some may claim that the Carnot cycle is of limited interest to chemists, we consider that the Carnot cycle is of such historical importance in the development of the Second Law that it cannot be overlooked. We believe that all chemists should have a solid understanding of the Carnot cycle. On the practical side, we are also aware that in many universities a large number of engineering students take junior-level chemical thermodynamics; therefore, one should include a thorough discussion of the Carnot cycle.

In our own experience, we have assigned our students to find a relation between temperature and volume along an adiabat for nonideal gases. Students immediately find that the typical textbook derivation for the ideal gas cannot be extended for several equations of state. To solve this problem, we give them access to most of this paper, where the key to the solution is the derivation of the entropy along an adiabat. Finally, we allow some students to consider the general case valid for any equation of state as an independent project, which counts towards their final grade.

In the next section we review Carnot’s reasoning, and in Section III we consider a general analysis of the Carnot cycle and its efficiency using general thermodynamic relationships applicable to any equation of state. In section IV we discuss our results.

Carnot Theorem

In contrast with Carnot’s reasoning, which used the principle of conservation of heat from the caloric theory, we start with the First Law, which considers that the total work performed by a cyclic engine is equal to:

$$W = -Q_H - Q_C \tag{1}$$

Here Q_H is the heat gained by the system from the hot reservoir, and Q_C is the heat lost by the system to the cold reservoir, that is, $Q_C < 0$. The engine efficiency, therefore, is the ratio between the work performed and the heat gained from the hot reservoir, that is,

$$\eta = 1 - \frac{|Q_C|}{Q_H} \tag{2}$$

Equation 2 is the so-called Carnot theorem.

In his work, Carnot argues that only reversible cycles are able to avoid heat losses due to temperature gradients between the system and the hot and cold reservoirs; thus, any real engine is prone to heat transfer. This heat transfer reduces the amount of heat available to do work. Consequently, the maximum efficiency is not achieved by real engines. Once we accept Carnot’s statement on the relation between reversibility and maximum efficiency, we have to consider that any reversible cyclic engine has to achieve the same maximum

S1430-4171(02)03555-7, Published on Web 05/10/2002, 10.1007/s00897020555a, 730127ep.pdf

efficiency. This corollary also implies that the maximum efficiency of any reversible cyclic engine is independent of the design and material properties of the engine; thus the maximum efficiency can only depend on the hot and cold reservoir's temperatures. In other words

$$\frac{|Q_C|}{Q_H} = f(T_C, T_H) \tag{3}$$

but this ratio has to satisfy the following relations:

$$\frac{|Q_1|}{Q_2} = f(T_1, T_2) \tag{4a}$$

$$\frac{Q_2}{Q_3} = f(T_2, T_3) \tag{4b}$$

$$\frac{|Q_1|}{Q_3} = f(T_1, T_3) \tag{4c}$$

As a consequence of eq 4, the function *f* also has the following property:

$$\frac{|Q_1|}{Q_3} = f(T_1, T_2) f(T_2, T_3) \tag{5}$$

These properties can be satisfied only if *f* is such that

$$f(T_C, T_H) = \frac{g(T_C)}{g(T_H)} \tag{6}$$

Therefore eq 3 reduces to

$$\frac{|Q_C|}{Q_H} = \frac{g(T_C)}{g(T_H)} \tag{7}$$

Now we have two options. We either follow Kelvin's path or use the ideal gas as the working substance for the reversible Carnot cycle. In the former, Kelvin defines the absolute or Kelvin scale where the ratio of absolute temperature is equal to the ratio of heat absorbed to the heat released in a reversible Carnot cycle. In the latter, authors use the design independence property, where the analysis of any particular reversible cyclic engine will give us an expression for the efficiency that is valid for any reversible cyclic engine. In particular most textbooks in physical chemistry [3–13] use the material properties of the ideal gas to study the reversible Carnot cycle. This analysis yields an expression that suggests the existence of an exact differential. In the process, this approach does not leave a sense of generality, because the relations used are only satisfied by the ideal gas; therefore, an alternative derivation valid for any equation of state is desirable.

Alternative Derivation of the Efficiency

In this section we discuss alternative analysis of a reversible Carnot cycle valid for any equation of state. We begin with a review of the reversible Carnot cycle:

a) gas with initial volume V_o is in contact with a hot reservoir at temperature T_H; the gas undergoes a reversible isothermal expansion reaching a final volume V_1.
b) In this step the system undergoes a reversible adiabatic expansion from T_H and V_1 to T_C and V_m.
c) Next, the gas undergoes a reversible isothermal compression from V_m to V_2.
d) Finally, the system undergoes a reversible adiabatic compression from T_C and V_2 to T_H and V_o.

Before we calculate Q_H and Q_C, we would like to find some helpful general thermodynamic relationships. First, we consider the First Law in its differential form for the internal energy *U*,

$$dU = dQ - P_{\text{ext}}\, dV \tag{8a}$$

where we are considering only PV work. Next, we consider a reversible process, thus we can rewrite eq 8a as:

$$dU = dQ - PdV \tag{8b}$$

where we have substituted for the external pressure, P_{ext}, by the internal pressure, *P*, given by the equation of state.

Next we use the general definition of specific heat to express *dU* as

$$dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{8c}$$

where

$$C_v \equiv \left(\frac{\partial U}{\partial V}\right)_V \tag{9}$$

In particular for an isothermal process, that is, $dT = 0$, and using eqs 8b and 8c, we can write the following relation:

$$dQ_{\text{iso}} = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \equiv F(V,T)\, dV \tag{10}$$

For an adiabatic process, $dQ = 0$, we get from eqs 8b and 8c:

$$C_v dT = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV = -F(V,T)\, dV \tag{11}$$

Now, with help of eqs 10 and 11, we can analyze a reversible Carnot cycle. First, we consider the isothermal expansion and find that the heat gained by the system as it expands from V_o to V_1 is given by

$$Q_H = \int_{V_o}^{V_1} F(V, T_H)\, dV \tag{12}$$

For the reversible isothermal compression, the heat lost is given by:

$$Q_C = \int_{V_\mathrm{m}}^{V_2} F\left(V, T_\mathrm{C}\right) dV \tag{13}$$

Using eqs 12 and 13, we find the following relation for the heat ratio:

$$\frac{Q_\mathrm{H}}{Q_\mathrm{C}} = \frac{\int_{V_\mathrm{o}}^{V_1} F\left(V, T_\mathrm{H}\right) dV}{\int_{V_\mathrm{m}}^{V_2} F\left(V, T_\mathrm{C}\right) dV} \tag{14}$$

Again eq 14 is general so it is satisfied by any equation of state.

For the reversible adiabatic expansion and compression we have the following relation:

$$C_v\left(V, T\right) dT = -F\left(V, T\right) dV \tag{15}$$

The adiabatic constraint reduces the number of independent variables. Thus, we could find, in principle, an expression of the temperature as a function of volume, that is, $T(V)$. In other words, T and V satisfy the following relation:

$$r\left(V, T\right) = \text{constant} \tag{16}$$

where r is a smooth function of V and T. Consequently, r has to satisfy the following differential relation:

$$\left(\frac{\partial r}{\partial T}\right)_V dT = -\left(\frac{\partial r}{\partial V}\right)_T dV \tag{17}$$

We can associate eq 15 with eq 17 by relating C_V and $F(V, T)$ to r, that is,

$$C_V = \left(\frac{\partial r}{\partial T}\right)_V \tag{18a}$$

$$F\left(V, T\right) = \left(\frac{\partial r}{\partial V}\right)_T \tag{18b}$$

If we want dr to be an exact differential, eqs 18a and 18b must also satisfy the following equation:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial F}{\partial T}\right)_V \tag{19}$$

Using eqs 9 and 10, we can reduce eq 19 to

$$\left(\frac{\partial P}{\partial T}\right)_V = 0 \tag{20}$$

which is not satisfied in general; therefore, eq 15 is not an exact differential.

As we can see, dQ is not an exact differential in general. In this case we turn to the theory of linear differential forms and the Caratheodory formulation of the Second Law, [15, 16] in which the possible existence of an integrating factor is considered. Without going into the more abstract and mathematical Caratheodory approach, we only consider an integrating factor, $\beta\,(V, T)$, such that

$$\beta C_V = \left(\frac{\partial r}{\partial T}\right)_V \tag{21a}$$

$$\beta F\left(V, T\right) = \left(\frac{\partial r}{\partial V}\right)_T \tag{21b}$$

$$\left(\frac{\partial \beta C_V}{\partial V}\right)_T = \left(\frac{\partial \beta F}{\partial T}\right)_V \tag{21c}$$

Moreover eq 21c reduces to a general partial differential equation for β,

$$C_V\left(\frac{\partial \beta}{\partial V}\right)_T - F\left(\frac{\partial \beta}{\partial T}\right)_V + \beta\left[\left(\frac{\partial C_V}{\partial V}\right)_T - \left(\frac{\partial F}{\partial T}\right)_V\right] = 0 \tag{22}$$

If we use eqs 9 and 10 in eq 22, we find

$$\frac{C_V}{F}\frac{1}{\beta}\left(\frac{\partial \beta}{\partial V}\right)_T - \frac{1}{\beta}\left(\frac{\partial \beta}{\partial T}\right)_V - \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_T + P} = 0 \tag{23}$$

where eq 23 has to be satisfied by β.

We should emphasize that integrating factors are not unique; therefore, we can try some simplifications. First, we assume that β is only a function of temperature, that is,

$$\beta \equiv \beta\left(T\right) \tag{24}$$

This assumption reduces eq 23 to

$$-\frac{1}{\beta}\left(\frac{d\beta}{dT}\right) = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_T + P} \equiv \frac{1}{f\left(T\right)} \tag{25}$$

where $f(T)$ is a smooth function of temperature. Second, we notice that for an ideal gas, $f(T) = T$, which means that $\beta_{ideal}(T) = 1/T$. Because all real gases approach the ideal gas behavior in the limiting case of infinitely low density, and infinitely large temperature, $f(T)$ should approach T in the limiting case. Consequently we could generalize and assume that

$$\beta\left(T\right) = \frac{1}{T} \tag{26}$$

But if we use eq 26 in eq 25, we find that the following condition also has to be satisfied:

$$T\left(\frac{\partial P}{\partial T}\right)_V=\left(\frac{\partial U}{\partial V}\right)_T+P \tag{27}$$

where $\left(\frac{\partial U}{\partial V}\right)_T$ is the so-called internal pressure. Also notice that eq 27 is a relation between the internal energy and the equation of state,

$$\left(\frac{\partial U}{\partial V}\right)_T=T^2\left(\frac{\partial}{\partial T}\frac{P}{T}\right)_V \tag{28}$$

Using eq 28, we find that the internal energy is given by [14]

$$U(V,T)=U_{\text{Ideal}}(T)+T^2\int_{\infty}^{V}\left(\frac{\partial}{\partial T}\frac{P(V',T)}{T}\right)_{V^1}dV' \tag{29}$$

where we consider the following reference condition

$${}_V\underline{\lim}_{\infty}U(V,T)=U_{\text{ideal}}(T) \tag{30}$$

Also, eq 27 transforms the heat ratio, eq 14, into

$$\frac{Q_{\text{H}}}{Q_{\text{C}}}=\frac{T_{\text{H}}}{T_{\text{C}}}\frac{\displaystyle\int_{V_o}^{V_1}\left(\frac{\partial P(V',T_{\text{H}})}{\partial T_{\text{H}}}\right)_{V'}dV'}{\displaystyle\int_{V_m}^{V_2}\left(\frac{\partial P(V',T_{\text{C}})}{\partial T_{\text{C}}}\right)_{V'}dV'} \tag{31}$$

Now, we can calculate $Cv(V,T)$ from eq 29 and find $r(V,T)$. First, the specific heat at constant volume is given by

$$C_V(V,T)=C_V^{\text{ideal}}+T\int_{\infty}^{V}\left(\frac{\partial^2}{\partial T^2}P(V',T)\right)_{V'}dV' \tag{32}$$

Notice that for any equation of state with a vanishing second partial derivative with respect to temperature, C_V is identical to the ideal gas case. Equation 32 can also be derived from eq 21c.

Using eqs (21c, 32), we find that $r(V,T)$ is given by

$$r(V,T)=\int_{T_{ref}}^{T}\frac{C_V^{\text{ideal}}}{T^1}dT^1+\int_{\infty}^{V}\left(\frac{\partial}{\partial T}P(V',T)\right)_{V'}dV'=\text{constant} \tag{33}$$

where we define a reference temperature as T_{ref}, and the following limiting conditions are required

$$\lim_{V\to\infty}\left(\frac{\partial}{\partial T}P(V,T)\right)_V=0 \tag{34}$$

$$\lim_{V\to\infty}\left(\frac{\partial^2}{\partial T^2}P(V,T)\right)_V=0 \tag{35}$$

All points on an adiabatic path satisfy the condition expressed by eq 33. For example, if we pick the beginning and ending points of the first adiabatic expansion in the Carnot cycle, we find

$$\int_{T_{\text{ref}}}^{T_{\text{H}}}\frac{C_V^{\text{ideal}}}{T^1}dT^1+\int_{\infty}^{V_1}\left(\frac{\partial}{\partial T_{\text{H}}}P(V',T_{\text{H}})\right)_{V'}dV'=\text{constant} \tag{36}$$

$$\int_{T_{\text{ref}}}^{T_{\text{C}}}\frac{C_V^{\text{ideal}}}{T^1}dT^1+\int_{\infty}^{V_m}\left(\frac{\partial}{\partial T_{\text{C}}}P(V',T_{\text{C}})\right)_{V'}dV'=\text{constant} \tag{37}$$

These two equations reduce to a final relation between points on the adiabatic path

$$\int_{T_{\text{C}}}^{T_{\text{H}}}\frac{C_V^{\text{ideal}}}{T^1}dT^1+\int_{\infty}^{V_m}\left(\frac{\partial}{\partial T_{\text{C}}}P(V',T_{\text{C}})\right)_{V'}dV'-\int_{\infty}^{V_1}\left(\frac{\partial}{\partial T_{\text{H}}}P(V',T_{\text{H}})\right)_{V'}dV' \tag{38}$$

In a similar way we find that the points (V_2, T_{C}) and (V_o, T_{H}) satisfy

$$\int_{T_{\text{C}}}^{T_{\text{H}}}\frac{C_V^{\text{ideal}}}{T^1}dT^1=\int_{\infty}^{V_2}\left(\frac{\partial}{\partial T_C}P(V',T_{\text{C}})\right)_{V'}dV'-\int_{\infty}^{V_o}\left(\frac{\partial}{\partial T_{\text{H}}}P(V',T_{\text{H}})\right)_{V'}dV' \tag{39}$$

Because the left hand side of eqs 38 and 39 are the same, we can rearrange them to get the following relation:

$$-\int_{V_{\text{o}}}^{V_1}\left(\frac{\partial}{\partial T_{\text{H}}}P(V',T_{\text{H}})\right)_{V'}dV'=\int_{V_{\text{m}}}^{V_2}\left(\frac{\partial}{\partial T_{\text{C}}}P(V',T_{\text{C}})\right)_{V'}dV' \tag{40}$$

Not only does eq 40 relate the four points that defined the adiabatic expansion and compression, but it also relates the points of the isothermal processes of the cycle.

Using eqs 40, 27, and 2, we get that the efficiency of a reversible Carnot cycle is

$$\eta=1-\frac{T_{\text{C}}}{T_{\text{H}}} \tag{41}$$

Equation 41 depends only on the reservoir's temperature. Also in our analysis one could use any of the equations of state; thus, this analysis in fact stresses the Carnot cycle's independence on material properties of the working substance.

Discussion

Our presentation, which is in the spirit of the Caratheodory approach [17], is complementary to the usual analysis of the reversible Carnot cycle using the ideal gas. Although our analysis is general and applies to any equation of state, it stresses the role of an integrating factor, β. In particular, we emphasize that $1/T$ is an integrating factor if and only if the following relation is satisfied:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{42}$$

As a consequence, $\beta\, dQ_{\text{rev}},$

$$\frac{dQ_{\text{rev}}}{T} = \frac{C_V(V,T)}{T}dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV \equiv dS \tag{43}$$

is an exact differential, which defines entropy. Usually, in the definition of entropy we include $1/T$ and assume that dS is an exact differential. From this assumption, as we can find in every textbook [2–13], we can derive eq 42. In other words, eq 43 is an exact differential if, and only if, eq 42 is satisfied.

In summary, our approach emphasizes the existence of an integrating factor, Carnot's statement on the material property's independence, and a relation between V and T for the adiabatic portions of the cycle as expressed by eqs 33, 38 and 39. The existence of the integrating factor implies an exact differential, and the general analysis includes any equation of state.

Acknowledgments. The author would like to thank the National Science Foundation for financial support (CHE-9312160 and CHE-0136143) and gratefully acknowledges Professor David Park for illuminating and stimulating discussions on thermodynamics.

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S1430-4171(02)03555-7, Published on Web 05/10/2002, 10.1007/s00897020555a, 730127ep.pdf