

Research Article

# Carnot Efficiency Used to Demonstrate a Second Law Fault in Defining Limits on Heat Energy Conversion

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## Abstract

A closed transcritical power cycle using an ethanol and 2-Naphthaldehyde solution as its working fluid provides a format for using Carnot efficiency to define conjectural second law limits on positive excess enthalpy of solution reactions and heat energy conversion. Changes in the solvent's density with resultant changes in solubility between the closed cycle's low and high temperatures establish an internal heat transfer where heat input near the cycle's  $T_2$  to satisfy the excess enthalpy reaction is transferred by retrograde solubility to near the cycle's  $T_1$  before it affects gas expansion. The effect of this heat transfer causes this closed cycle's  $Q$  efficiency to exceed the Carnot  $T$  efficiency of its input heat.

## Keywords

Second Law, Solution Thermodynamics, Solubility, Ethanol, Closed Power Cycle

## 1. Introduction

During the nineteenth century the second law developed from an observation and an assumption. The observation became its foundation in the fact that Carnot efficiency defines the maximum rate heat energy can be converted to work between two temperature levels of an absolute scale by a gas's cyclical expansion and contraction in a closed cyclical process. From this fact the assumption ensued that this maximum rate of heat to work conversion by gas expansion-contraction, or Carnot efficiency, has influence that extends beyond its own simple physics to establish a universal limit on the convertibility of heat to work by all closed two  $T$  cyclical processes, resulting in the labeling of heat as a unique lowest energy form [1].

The molecular thermodynamic proportionalities evidenced by Trouton's constant, boiling point to critical temperature ratios, and the thermal proportionality of Carnot efficiency are

used to craft a formulation for predicting maximum transcritical positive excess enthalpy of solution differentials. It is demonstrated that the second law fails to correctly predict maximum excess enthalpy differentials and the cycle's  $Q$  efficiency exceeding the  $T$  efficiency of its input heat invalidates the assumption that heat is a lowest form of energy.

## 2. Discussion

A 110kJ positive molar excess enthalpy of solution reaction is found between ethanol and 2-Naphthaldehyde [2]. Ethanol has a density of .789g/mL. Calculations using REFPROP data are in kJ/kg so the 110kJ molar value converts to  $1/.789 \times 110\text{kJ} = 139.4\text{kJ}$  per kg. The curve in Figure 1, from Ref. 2, (round symbol), shows the change in the rate of change in

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Received: 2 January 2025; Accepted: 21 January 2025; Published: 10 February 2025



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solubility where mole fraction solubility increases from 1.164 to 31.38 over a 25 degree temperature rise from 283.15K to 308.15K at 0.1 MPa. The assumption is made here that in projecting this curve another 177 degrees to ethanol's temperature and density conditions of 485K and 523.9kg/m<sup>3</sup> at point A of the cycle depicted on the P-h diagram in Figure 2, at least one gram mole of 2-Naphthaldehyde (molecular weight 156.18 and melting temperature of 563K) will be dissolved.

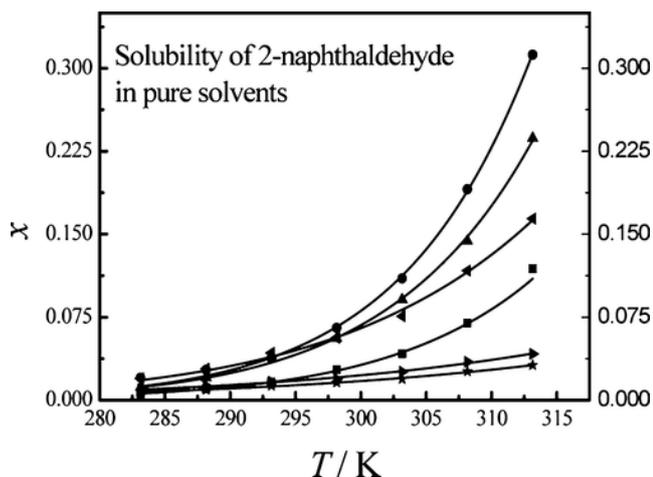


Figure 1. Solubility diagram.

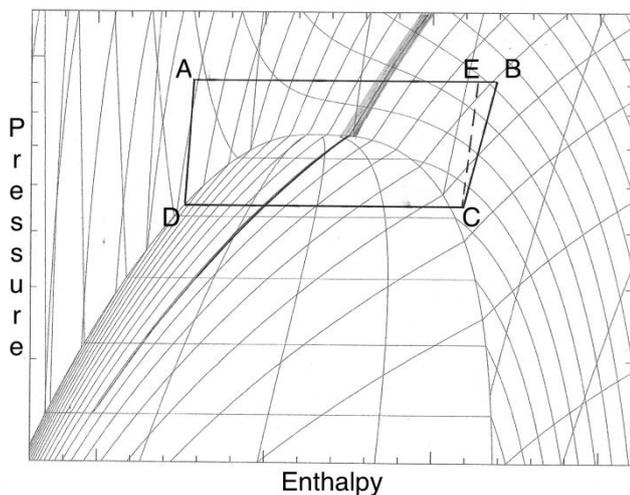


Figure 2. p-H diagram.

After a molar solution reaction is complete at point A, more heat is added at constant pressure from ascending thermal reservoirs bringing the solution to point E. Adiabatic expansion then proceeds from E to a density of 63.72kg/m<sup>3</sup> at point C. Based on the difference in solvent density from A to C, solubility differentials typically range from a low of about 10 to 1.0 to over 1000 to 1.0. The literature abounds with research data on solubility verses solvent density that support

this observation. A few examples are given in references 4-10. Though solubility at the density at C can be less than one percent of the maximum for the cycle found at point A, for purposes of discussion, a second assumption is made that about 17.6% solubility, or 20.85kJ of the positive excess enthalpy found at A will remain at point C. This means that 118.49kJ of the original 139.4kJ was returned as heat to the expanding solvent as the solute molecules rebonded between A-E-C. The shaded constant density line on Figure 2 shows the solvent density range where most retrograde solubility occurs [3-22]. Transferring solubility data presented in table form from each of these nineteen references to that solvent's p-H diagram clearly shows the pattern of retrograde solubility related to solvent density.

During the adiabatic expansion that occurs between E and C, (broken line) the solute molecules will contribute about 5kJ of sensible heat from (Kopps nos.) and about 20kJ rebonding energy to the expansion. These values are used in the Carnot efficiency calculations. Isobaric condensation occurs from C to D and adiabatic compression returns the solution to A. Increasing or decreasing the 20kJ contributed to adiabatic expansion only marginally affects the Q efficiency to T efficiency ratio described below.

Connecting points A, E, C, and D defines a closed power cycle. Carnot efficiency can then be used to compare the input heat's second law work potential to the cycle's actual work output. The 118.49 kJ of energy input at 480-485K, (mostly at 480K) to facilitate the positive excess enthalpy of solution reaction supplants heat otherwise input from the ascending thermal reservoirs during expansion from A to C. Most of this heat would come from the ethanol's condensation from C to D at 480K as it approached the saturated liquid state at D.

The 118.49kJ of heat input at 480K to satisfy the solution reaction near the cycle's T<sub>2</sub>, point D has, by the Carnot cycle, 480K-480K/480K = 0, no potential to do work in a closed power cycle. Because heat input from A to E comes from ascending thermal reservoirs, the Carnot T<sub>1</sub>-T<sub>2</sub>/T<sub>1</sub> work potential for the heat input from each reservoir can be calculated separately and then summed to determine the maximum second law allowed work output potential for the total heat input to this closed cycle. This value is compared to the cycle's actual Q<sub>1</sub>-Q<sub>2</sub>/Q<sub>1</sub>.

The conjectural, or second law determined T<sub>1</sub>-T<sub>2</sub>/T<sub>1</sub> maximum work output for the cycle is 31.31kJ, Table 1, while the cycle's actual work output is 40.34kJ as determined from + (ΔH - ΔU) from A to E, + (ΔU) from E to C, - (ΔH - ΔU) from C to D, and -ΔU from D to A, Table 2. The internal heat transfer from the solubility differential enables the closed cycle to achieve a Q efficiency 1.29 times the Carnot T efficiency potential of its input heat. Ethanol state point data is on Table 2 [23].

**Table 1.** Carnot work output.

Temp. K	Carnot Eff.	Input kJ	Work
480.00	0.00	118.49	0.00
510.85	.0506	101.00	5.11
526.41	.0787	101.00	7.95
536.91	.0967	101.00	9.76
540.60	.1028	27.5 + 40	2.83
553.22	.1230	46 + 40	5.66
			31.31

**Table 2.** Ethanol state point data from REFPROP 10.

Temp. K	Pressure (MPa)	Density (kg/m <sup>3</sup> )	Int. Eng. (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)	Quality (kg)
(D)485.00	3.7288	523.90	497.27	504.39	1.1872	.00000
(A)490.47	9.2	552.11	497.86	514.53	1.1872	
(B)556.63	9.2	173.14	957.36	1010.50	2.1266	
(C)486.92	3.7288	63.72	901.49	960.01	2.1266	
(E)510.85	9.2	493.53	595.89	614.53	1.3868	
526.41	9.2	413.10	692.26	714.53	1.5795	
536.91	9.2	314.57	785.28	814.53	1.7675	
540.60	9.2	272.05	825.71	859.53	1.8510	
553.22	9.2	185.12	935.80	985.50	2.0816	

### 3. Conclusion

If the assumption made in the 1800s about the nature of heat was correct, this cycle format and Carnot efficiency would be able to determine the maximum positive excess enthalpy of solution differential that can exist between points A and C in any solvent. Sustaining the second law's certainty requires its being able to contradict the data presented here and demonstrate that the excess enthalpy of solution differential of 2-Naphthaldehyde in ethanol between points A and C will not exceed about 24kJ. Any amount of internal heat transfer by the differential in excess heats of solution above 24kJ invalidates the assumption by causing the cycle's Q efficiency to exceed its T efficiency. The 118.49kJ of internal heat transfer supported by established patterns of solubility challenges the second law. An alternate requirement of the second law would be that the amount of 2-Naphthaldehyde left in solution at the solvent

density of 63.72kg/m<sup>3</sup> at point C must be at least 75% of a gram mole, not the 10% to 0.01% normally found. For heavier low boiling point compounds like R14 this second law maximum positive excess enthalpy of solution differential in an equivalent cycle becomes irreconcilably small at about 6kJ in R14 and about 15.5 kJ in CO<sub>2</sub>. If this is a fault in the second law then the complete exhaust heat regeneration process described in reference [22] makes ambient heat an accessible energy source. The premise of this discussion can be either proven or disproven with excess enthalpy of solution tests at the conditions of density and temperature at points A and C.

### Author Contributions

David Van Den Einde is the sole author. The author read and approved the final manuscript.

## Data Availability Statement

All data used is in the public domain.

## Conflicts of Interest

The author declares no conflicts of interest.

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