

Complete power cycle exhaust heat regeneration and second law logic

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Abstract: It is demonstrated, given a sufficiently large positive excess enthalpy of solution reaction between a molecular solid solute and a low boiling point solvent, that the differential in excess enthalpies of solution between the reaction in the solvent's dense liquid and expanded supercritical states will enable the solution, when used as the working fluid in a closed condensing power cycle, to attain complete exhaust heat regeneration. Xenon is used as the solvent to demonstrate the potential. Errors in 18th century logic that helped establish the second law are explained. © 2020 *Physics Essays Publication*. [<http://dx.doi.org/10.4006/0836-1398-33.2.159>]

Résumé: Il est démontré, étant donné un excès positive suffisamment grand d'enthalpie de réaction en solution entre un soluté moléculaire solide et un solvant à bas point d'ébullition, que le différentiel en excès d'enthalpie de solution entre la réaction dans le liquide dense du solvant et les états supercritiques expansés permettra que la solution, lorsqu'il est utilisé comme fluide de travail dans un cycle de puissance de condensation fermé, d'atteindre une régénération complète de la chaleur de sortie. Le xénon est utilisé comme solvant pour démontrer le potentiel. Les erreurs dans la logique du XVIIIe siècle qui ont aidé à établir la deuxième loi sont expliquées.

Key words: Second Law; Logic; Thermodynamics; Power Cycle; Retrograde Solubility; Exhaust Heat Regeneration; Entropy.

I. INTRODUCTION

Improvements to the cycle presented in Ref. 1 are described that simplify its exhaust heat regeneration processes and increase its work output. In that cycle, a 42 kJ positive excess enthalpy of solution value was used in calculations. This 42 kJ value required that the cycle use an evaporative refrigeration process to regenerate a portion of its exhaust heat. It is shown, here, that if a 62 kJ positive excess enthalpy of solution reaction can be achieved between liquid xenon and a molecular solid solute, the excess enthalpy differential between the reaction in the solvent's dense liquid state and expanded supercritical state will allow the cycle to attain complete exhaust heat regeneration without the evaporative refrigeration portion of the regeneration process.

The thermodynamics of solvent–solute interactions considered in this paper are limited to induced polarities or the London dispersion forces of nonpolar solvents. No research has ever been done to determine how large a positive excess enthalpy of solution reaction can be achieved in a heavy low boiling point nonpolar compound like xenon. Reference 2 demonstrates positive molar excess enthalpies of 264.64 kJ for tris-(2,4-ditert-butylphenyl)-phosphite in the solvent ethyl butyrate, 259.79 kJ in the solvent N-hexane, and 230.55 kJ in the solvent N-heptane. Like xenon, these solvents are nonpolar and have molecular weights of 116.16, 86.16, and 100.21, respectively. The implication is that the 62 kJ value used in these calculations appears well within the range of an attainable value. The refrigerants R-14 and R-125 also exhibit the thermodynamic properties required to

function in this cycle. Errors of logic that originally helped establish the second law in the 1800s are explained.

II. DISCUSSION

Three factors that contributed to the development of the second law were a law of physics, an assumption, and a conclusion of logic based on that assumption. First, the law of physics is the fact that Carnot's T_1-T_2/T_1 expresses the maximum rate that heat can be converted to work by the expansion and compression of an ideal or real gas between two temperature levels of an absolute scale. This is an absolute law of physics. It would require a first law violation or a creation of energy for any cycle that relies solely on a gas's expansion and compression to exceed this rate of energy conversion.

Next, the assumption was made that the rate the ideal gas Carnot cycle can convert heat to work defined the maximum heat to work conversion potential for all possible $2T$ cyclical processes, regardless of how far their internal energy conversions and transfers diverged from the simple expansion and compression of a gas. Finally, based on this assumption, errors in logic, and the lack of contradicting evidence, a conclusion was reached that heat must be a unique lowest form of energy to which all other forms degrade.

The errors of logic that supported this conclusion center on the use of the term efficiency. A tacitly accepted parity of two meanings of the term led to the logic error of false equivalency. The uncontested definition of the term efficiency is the fact that no real process can operate without inefficiency. The Carnot cycle is perfectly reversible and because no process can be more efficient than a perfectly

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reversible process, the cycle's heat to work conversion rate was assumed the most efficient possible; hence, any process that converted heat to work at a higher rate would have to exceed 100% efficiency. The assumption thus gained support from this tacitly accepted equivalency of definitions to lend a false significance to the concept of entropy.

Clausius defined a scale that measures the decrease in the availability of heat to do work as it passes from a higher to lower temperature reservoir without doing work at the rate it could have been converted to work by the expansion and compression of a gas in the Carnot cycle.³ Entropy was integrated into the false equivalency to support the assumption as follows: because no process can operate without inefficiency and no process can be more efficient than the perfectly reversible Carnot cycle, entropy, as a measure of inefficiency, must increase in all 2T heat to work conversion processes. If entropy did not increase, the assumption holds, any closed cyclical heat to work conversion process that converted heat to work between T1 and T2 at a rate greater than the Carnot cycle's T1-T2/T1 rate must incorporate or generate some form of perpetual motion. The tacit acceptance of the assumption that the perfectly reversible Carnot cycle's heat to work conversion rate or efficiency defined the maximum rate of heat to work conversion for all 2T cyclical processes thus sanctioned the conclusion that entropy must increase for all 2T processes as a proof of the assumption.

The truth or fallacy of the conclusion concerning the significance of Clausius's entropy scale relies entirely on whether or not the original assumption is correct. If the assumption is correct, the equivalent uses of the term efficiency are appropriate and entropy is a valid measure of some metaphysical reality that makes heat a unique lowest form of energy. If the assumption is incorrect, then entropy need not increase in all closed 2T cyclical processes. Merely equating the term inefficiency with entropy to tacitly shift efficiency's meaning from the incontrovertible to the presumed meaning does not prove the assumption.

This error of false equivalency generates the error of petitio principii where the premise of an argument, in this case the assumption, serves as a proof of a conclusion based on that assumption. As one early author suggested: each time we traverse this path of reasoning, it makes the proof even stronger. Some modern day theorists have extended this circular argument by asserting that the entropy scale can now be used to mathematically prove the assumption.

Recent research in RESS technology, supercritical solution thermodynamics, and the expanded database in REFPROP 10⁴ have eliminated the lack of contradicting evidence by generating sufficient empirical data to mount a simple challenge to the assumption. This xenon cycle, supporting explanations, and data in Refs. 5–7 demonstrate that perpetual motion of the second kind does not automatically generate perpetual motion of the first kind.

In this cycle, Carnot's T1-T2/T1 limit applies to how much heat to work the gas can convert during its expansion from the temperature at which the heat initially affects the gas's expansion to the temperature at which the heat is exhausted during condensation, but that conversion limit does not limit the magnitude of positive excess enthalpy of solution reactions, differentials in excess enthalpies of solution between a solution reaction in a solvent's dense liquid and expanded supercritical state, nor the amount of input heat energy that can thus be internally transferred from near the cycle's low temperature to near its high temperature before that energy affects gas expansion.

The first significant change to the cycle described in Ref. 1 is depicted on the generic P-h diagram where a second stage of adiabatic compression is added from C to D. In this range of compression, the solvent density is still high enough to avoid retrograde solubility.⁶ This second stage of compression increases the pressure and temperature at point F to increase the work output potential during adiabatic expansion from F to G. The change permits selecting the pressure and temperature range from B to C where exhaust heat regeneration can be accomplished with the lowest temperature rise of the cold condensed xenon-solute working fluid while it serves as a heat sink for its paired cycle's regenerated exhaust heat. As described in Ref. 1, the process requires two cycles operating in sync so that each uses the others cold condensed working fluid as the heat sink for its exhausted heat energy. The 62 kJ positive excess enthalpy simplifies the cycle by eliminating the need for the evaporative refrigeration portion of the regeneration process. The cycle proceeds as follows with the xenon state point data given in Table I, and the work inputs and outputs shown in Table II.

It is first assumed that 25 kJ of the 62 kJ positive excess enthalpy occurs from H to A. This reduces the solution's temperature from 260 K to 199 K. Adiabatic compression then occurs from point A to B raising the solution's pressure and temperature to 6 MPa and 200.64 K at B. From B to C,

TABLE I. Xenon state point data.

| | Temperature (K) | Pressure (MPa) | Density (kg/m ³) | Int. energy (kJ/kg) | Enthalpy (kJ/kg) | Entropy (kJ/kg K) | Quality (kg/kg) |
|---|-----------------|----------------|------------------------------|---------------------|------------------|-------------------|-----------------|
| H | 260.00 | 3.0820 | 2111.4 | 35.808 | 37.268 | 0.17039 | 0.00001 |
| A | 199.00 | 3.0820 | 2721.2 | 11.135 | 12.268 | 0.06177 | |
| B | 200.64 | 6.00 | 2730.4 | 11.141 | 13.338 | 0.06177 | |
| C | 254.55 | 6.00 | 2261.7 | 31.239 | 33.892 | 0.15210 | |
| D | 266.30 | 16.0 | 2319.4 | 31.357 | 38.256 | 0.15210 | |
| E | 316.92 | 16.0 | 1803.2 | 51.122 | 59.995 | 0.22656 | |
| F | 466.80 | 16.0 | 641.81 | 97.396 | 122.33 | 0.39175 | |
| G | 260.00 | 3.0820 | 280.89 | 83.850 | 94.822 | 0.39175 | 1.000 |

TABLE II. Work input and output.

| | Work (kJ/kg) $\Delta H - \Delta U$ | Work (kJ/kg) ΔU | Work (kJ/kg) |
|-------|---------------------------------------|----------------------------|--------------|
| A–B | | | –2.24 |
| B–C | Ignored | | |
| D–F | +18.035 | | |
| F–G | | +13.546 | |
| G–A | –9.84 | | |
| Gross | +31.581 | | |
| | –12.08 | | |
| Net | +19.5 | | |

one cycle's heat of condensation exhausted at 260 K from G to H is regenerated to the solution of the paired cycle via a simple heat exchanger. This is a dynamic process that transfers 57.554 kJ of one cycle's exhaust heat warming the paired cycle's solution from point B to C. It is dynamic in the sense that as solubility increases with the increase in pressure and temperature from A to B to C, the solution receiving heat that goes to supplying its excess enthalpy requirements will increase slowly in temperature until the reduction in the solvent density becomes the predominant influencing factor on solubility. Examples of how pronounced this increase in solubility from A to B to C can be with the increase in temperature is prevalent in the literature and demonstrated in Ref. 8.

What must be noted in Ref. 1 is the solubility curves demonstrated in Figs. 4 and 5. Consider N-heptane in Fig. 5 and Table 2. Over the 40 K temperature rise from 280 K to 320 K, the solubility increased from 0.01 to 0.033. The temperature equivalent for N-heptane at the xenon cycle's point D of is about 520 K. By projecting the curve of increase in solubility shown in Fig. 5 another 200° from 320 K to 520 K and 3 MPa, it is safe to predict, based on the observed increase in solubility with the increase in temperature in this temperature and solvent density range, that enough solubility increase could be expected with a nonpolar solvent to attain the 62 kJ value needed for this xenon cycle to function.

Adiabatic compression next proceeds between C and D. From D to E, about 31 kJ of external heat is input. With further external heat input beyond E, retrograde solubility will initiate as solvent density is reduced. It should be noted as in Ref. 1 that this retrograde solubility will become spontaneous as each kJ returned as heat will, in this range of expansion, cause about a 2° temperature rise and as the solution continues to expand, the proportioning of energy between the molecule's internal freedoms and translation energy continues to shift toward the translational.

Energy from the solute's rebonding and its sensible heat contribution to xenon's expansion from F to G causes a quasi-isothermal-adiabatic expansion shown as the dashed line on Fig. 1. The rate of solute rebonding through this range of xenon's expansion makes it impossible, without specific empirical data per solvent–solute combination to determine at exactly what temperature expansion needs to initiate at G to terminate at H. Suffice to note that there will

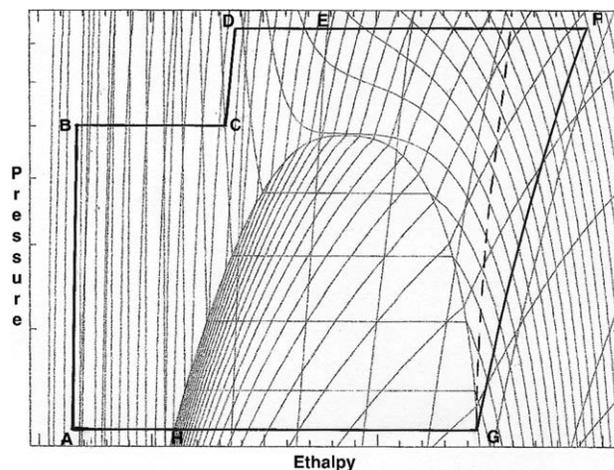


FIG. 1. Power cycle plot on the generic P-h diagram.

exist a path of expansion from some temperature at G that will terminate at H.

The point to be stressed here is that it does not matter at what exact temperatures the retrograde solubility occurs in the E to F to G range. If more than 31 kJ external heat input near point E (approximate gross work output per cycle) is required to reach a solvent density at which retrograde solubility initiates, it will merely cause the 62 kJ value of energy returned to xenon as heat from the solute's rebonding to increase the temperature of the working fluid above the temperature from which the quasi-isothermal-adiabatic expansion must initiate for the expansion to terminate at point G. But at this point in the cycle, any excess heat returned from solute rebonding above that temperature can simply be exhausted near point F (466 K). The determining factor of how much heat, 31 kJ more or less, needs to be introduced to each cycle between D and E is established by how much energy is converted by the quasi-isothermal-adiabatic expansion. Once heat is no longer deemed a unique lowest form of energy, the exact temperatures at which these heat exchanges occur becomes irrelevant.

Suffice to acknowledge that the majority of the heat energy supplied to accomplish the positive excess enthalpy of solution reaction from points H to A to B to C was introduced near the cycle's T2. As such it had, by the second law, no potential to do work in the cycle. The only factor from the second law's development that is relevant to this process is the fact that Carnot's T1-T2/T1 gas expansion–compression heat to work conversion limit applies to the temperature differential between each T1 temperature from which the regenerated heat affects gas expansion and the T2 condensation temperature. The key to the cycle's utility is that a 62 kJ excess enthalpy differential enables it to accomplish complete exhaust heat regeneration while using an ambient heat source.

III. CONCLUSION

The rate a gas's expansion and compression can convert heat to work and the fact that nothing moves without inefficiency was two laws of physics woven together in a

circular argument to support an assumption that has served as the foundation of the second law. For the lack of contradicting evidence, this assumed law has been taught to each successive generation of scientists as a profound fundamental law. All the factors that are required for this cycle to function, such as the existence and magnitude of positive excess enthalpy of solution reactions, supercritical retrograde solubility, and the fact that the excess volume portion of a positive excess enthalpy change can be positive, neutral, or negative are confirmed in the literature. The only unknown is how large can a positive excess enthalpy of solution reaction be in a heavy low boiling point compound like xenon. Considering that 230 kJ to 266 kJ plus positive molar excess enthalpy of solution reactions for heavy nonpolar solvents have been found in research that was not focused on what maxima can exist with the inclusion of cosolvents and entrainers, it is illogical to claim that the energy conversion rate attainable from a gas's expansion and compression between T1 and T2 can somehow prevent xenon, R-14, R-125, or any other heavy, nonpolar, low boiling point

compound from generating a positive excess enthalpy of solution reaction sufficient to accomplish this exhaust heat regeneration process. If this large positive excess enthalpy of solution reaction with xenon can exist, then the second law loses its profound fundamental significance and the potential to tap into ambient heat as an energy source can be exploited.

¹D. Van Den Einde, *Phys. Essays* **32**, 300 (2019).

²J. Yang, B. Hou, J. Huang, X. Li, B. Tian, N. Wang, J. Bi, and H. Hoa, *J. Mol. Liquids* **283**, 713 (2019).

³R. Clausius, "On the application of the theorem of the equivalence of the transformation to the internal work of a mass of matter, benchmark papers on energy/5," in *The Second Law of Thermodynamics*, edited by J. Kestin (Dowden, Hutchinson, and Ross, Stroudsburg, PA, 1976), p. 329.

⁴National Institute of Standards and Technology, *REFPROP Version 10* (National Institute of Standards and Technology, Boulder, CO, 2018).

⁵D. Van Den Einde, *Appl. Phys. Res.* **10**, 5 (2018).

⁶D. Van Den Einde, *Phys. Essays* **29**, 207 (2016).

⁷D. Van Den Einde, *Phys. Essays* **30**, 224 (2017).

⁸X. Zhang, G. Qian, R. Wang, X. Yang, L. Hoa, H. Wei, and X. Zhou, *Fluid Phase Equilib.* **388**, 59 (2015).