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On Thermodynamic Peculiarities of the Absorption Heat Transformers

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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Short Research Article

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ABSTRACT

In this paper we describe the peculiarities of the thermodynamics of the absorption heat transformers (AHTs) pointing to the possibility of examining the AHT models from the standpoint not only of the equilibrium thermodynamics, as it usually is, but also of the non-equilibrium one. In the well-known models of absorption refrigerators commonly represented by a combination of the reversible Carnot cycles, the absorption effects are not taken into account. At that, the mechanical energy required for operation of the refrigerator in such a model is superior to its real value, such as in cycles with solutions of H_2O / LiBr and NH_3 / H_2O in several times. The examination of another AHT model represented by new cycles for a concurrent generation of electric power and cold shows that it also does not quite correlate with the earlier known models of the equilibrium (classical) thermodynamics. The evaluation of the performance of such cycles with the CH_3OH/LiBr and NH_3/$LiNO_3$ solutions shows that under certain circumstances it can exceed the performance of the corresponding Carnot cycles. The application in this event of the non-equilibrium thermodynamics to a greater extent conforms to the physical model of the absorption cycles and creates prerequisites for further improvement of the performance of the combined cycles for generation of energy and cold.

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1. INTRODUCTION

Nowadays the absorption heat transformers in which solutions of low-boiling (refrigerants) and high-boiling (absorbents) components are used as working fluid find application for the conversion of low-grade heat energy into other useful forms of energy, for example the electric power [1] or the heat energy of desired temperature level [2,3]. These systems are distinguished by a reduced consumption of mechanical energy (work) in comparison with the refrigerators in which gaseous or vaporous substances are used as working fluid.

Nevertheless, the models of various energy cycles, particularly such as the cycles of heat engines (HEs), vapor-compression (VCHTs) and absorption (AHTs) heat transformers are treated from the general standpoint of classical thermodynamics where the maximum efficiency of the equilibrium thermomechanical conversions is limited according to the second law of thermodynamics by the relative temperature difference of hot and cold external heat sources [4,5]. Such an approach agrees satisfactorily with the current practice as regards the cycles having substantially thermomechanical interactions, for example, of heat engines (HEs) or vapor-compression heat pumps (VCHPs).

However, this approach can turn out to be inadequately complete regarding the AHT cycles because of the availability in them of not only thermomechanical, but thermochemical interactions as well.

In principle, such systems can prove to be non-equilibrium and irreversible, allowing departures from the well-known temperature constraints of the Carnot cycle.

Therefore, further examination of the peculiarities of the thermodynamical AHT models may be of both theoretical and practical interest.

2. PECULIARITIES OF MODELS OF ABSORPTION REFRIGERATORS

Various models characterizing the operating principles of absorption heat transformers are known at the present time [6]. One of them shown in Fig. 1 is represented by the cycle of decreasing AHT or, otherwise, three-temperature forward cycle.

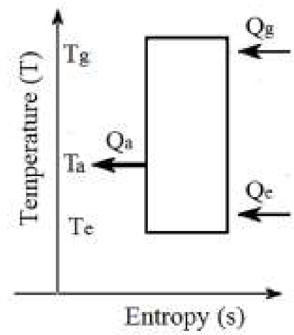

Fig. 1. Three-temperature forward cycle

Though such a model does not contain quantitative assessments of the AHT indices, it reflects the main peculiarities of such absorption cycles, and in particular the absence in such a cycle of the heat engine with the availability not of two, as it usually is, but of three heat sources. In so doing the hot and cold heat sources with T_g and T_e temperatures respectively are used for a concurrent delivery of heat energy to the system. Therewith the third heat source with the intermediate temperature T_a being approximately equal to the environmental temperature T_{envir} ($T_a \geq T_{envir}$) serves for re-injection of heat energy from the system. In comparison with other cycles of classical thermodynamics in which the absorption processes are absent, such an arrangement of heat flows (sources) is not quite conventional because the commonly employed separation of cycles into the direct (heat engines) and reverse (refrigerators) ones does not hold in this instance. Besides, the absence in such a cycle of the heat engine suggests the availability in it of the internal energy sources associated with the chemical interactions of solutions and with the absorption phenomena.

In another well-known model with the analogous arrangement of heat sources [5,7] having obtained a wide circulation, the mode of operation of the absorption cycles is proposed to be treated from the standpoint of the classical thermodynamics. In that event the internal energy sources in the absorption processes are disregarded, and as low energy source needed for the transformation of heat in the low temperature range ($T_a - T_e$) one suggests to employ an additional heat engine whose temperature interval $(T_g - T_a)$ involves higher temperatures of the available spectrum $(T_g - T_e)$.

Traditionally, such a model of absorption cycles is represented as a combination of ideal direct and reverse Carnot cycle whose diagram in the T (temperature) – S (entropy) coordinates appears in Fig. 2.

A comparison of the models under consideration shows that various mechanisms of absorption cycles have been proposed in them. Along with this, the results of application of the second of them, in which the absorption phenomena are disregarded, in a number of cases apparently cannot quite correlate with the experimental data.

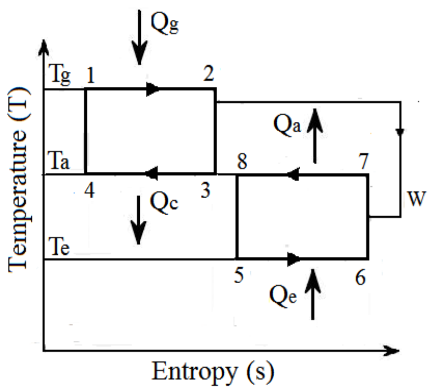

Fig. 2. The theoretical model of AHTs in the form of a combination of ideal Carnot cycles

Thus, for example, the maximum quantity of work W produced by the heat engine of the reversible Carnot cycle (1234 cycle in Fig. 2) in the temperature range $(T_g - T_a)$ can be determined from the Eq. (1) [5,7]:

$$W = Q_g\,(T_g - T_a)/T_g \tag{1}$$

in which Q_g is the heat consumed by the heat engine Carnot at T_g.

In this case the coefficient of performance of the Carnot cycle refrigerator (5678 cycle in Fig. 2) in the temperature range $(T_a - T_e)$ characterizing the relation of the amount of the generated cold to the quantity of work consumed therewith W is usually defined by the Eq. (2):

$$COP_c = Q_e/\mathrm{W} = T_e/(T_a - T_e) \tag{2}$$

in which Q_e is the heat consumed by the cycle at T_e.

In turn, the similar index of an absorption refrigerator may be defined as the ratio

$$COP_a = Q/N \tag{3}$$

wherein Q represents cooling capacity of the refrigerator, and N - its consumed power.

The relation of the coefficients of performance (COP_a/COP_c) of some absorption (single-effect and double-effect) refrigeration systems (according to the data of [6]) with corresponding refrigerators based on using the reversible Carnot cycles with the same temperature range $(T_a - T_e)$ is given in Table 1.

The data listed in Table 1 suggest that the consumption of mechanical energy in the absorption thermal transformers can be by several orders of magnitude less compared to a similar amount minimum required in the reversible refrigerator of Carnot cycle.

So small values of work consumed in the AHT cycles merely for the circulation of solution point up to a possibility of the transformation of heat to a higher temperature level only due to the properties of the solutions even without expenditure of mechanical energy.

Such a possibility, even if disregarded in the AHT model commonly represented by the cycles in Fig. 2, none the less is recognized as actually existing [5,6] and shows up when displaying the characteristic schemes of similar systems which are represented in Fig. 3.

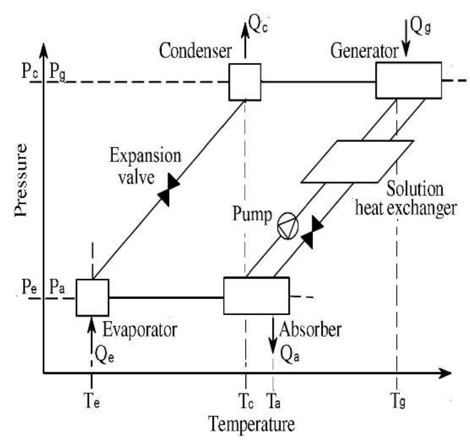

Fig. 3. Basic single-effect absorption cycle in Duhring plot

Table 1. The relation of the coefficients of performance of some absorption refrigeration systems (COP_a) and a thermomechanical refrigerator with the reversible Carnot cycle (COP_c)

Name of the system	T_e, ℃	T_a, ℃	Q, kW	N, kW	COP_a /COP_c
Single-effect NH_3/H_2O absorption cycle [6]	5.1	40.5	1760	12.4	18.2
Double-effect H_2O/LiBr absorption cycle [6]	5.0	2.4	1760	0.39	619.4

At the same time, for the VCHT model using a mechanical compressor similar temperature difference of the working fluid may be obtained through an increase of its pressure between the evaporator and condenser by means of the compressor, as it is illustrated in Fig. 4.

Such a difference of the modes of operation of AHT and VCHT is just attained owing to the employment in the AHT scheme (Fig. 3) of a chemical compressor incorporating an absorber, a pump, a heat exchanger of solution, a generator of vapor and an expansion valve, and not of a mechanical one, as is in the VCHT scheme.

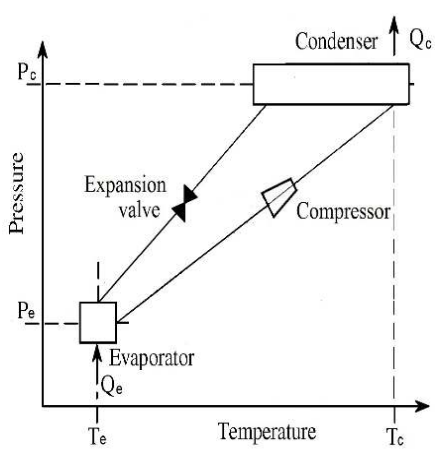

Fig. 4. Basic diagram of a vapor-compression refrigeration cycle in Duhring plot

In such a chemical compressor the possibility exists of increasing the temperature of the working fluid at the expense of internal energy sources (chemical potentials) emerging in a change of the concentration of solutions even without the use of the external sources of mechanical energy.

So, the well-known assumption of the classical model about a possible similarity of the absorption and thermomechanical refrigerators, based on the second law of thermodynamics, encounters certain difficulties.

3. PECULIARITIES OF THE MODEL OF ABSORPTION HEAT ENGINES (AHEs)

A reduction in the amount of mechanical energy consumed in the cycles of absorption refrigerators as compared with the Carnot cycle, noted above, determines the theoretical possibility of devising new absorption heat engines (AHEs) in which as distinct from other cycles of classical thermodynamics the useful temperature range of the cycle can surpass the temperature difference of heat sources, and the generation of electric power is allowable also in the region of temperatures lesser than the environmental temperatures.

In this case a concurrent generation of both electric power (work) and cold is allowable. Nowadays a number of publications [8–13] has been already devoted to the investigation of such AHE cycles. However, no increase in the efficiency (performance) of the AHE cycles akin to that observed in the cycles of absorption refrigerators has been yet revealed in these investigations.

Such a state of affairs appears to be associated with the choice therewith mainly of aqua-ammonia solutions as well as with a distinction of the comparing conditions of the Carnot cycle and the AHE cycle, in the latter of which the energy losses of various kinds connected with irreversibility and non-equilibrium of such cycles are also taken into consideration. At the same time, along with the examination of the AHE model from the standpoint of equilibrium thermodynamics it is also possible to treat it from the standpoint of non-equilibrium thermodynamics [14] in which the possibility is available of improving the efficiency of the system as the result of the influence of non-equilibrated energetic (e.g. chemical) potentials.

For a quantitative assessment of such a possibility let us compare the coefficients of performance of the reversible Carnot cycle η_c and of the single-effect AHE cycles η_a with the use as working fluid of the methanol

(CH_3OH) / lithium bromide (LiBr) and ammonia (NH_3) / lithium nitrate ($LiNO_3$) solutions, with the corresponding temperatures of heat sources being equal. The schematic diagram of one of such AHE cycles is shown in Fig. 5. Such an AHE cycle incorporates an expander (turbine) and a chemical compressor in which the vapor generator of such a compressor is connected to the inlet of the turbine and the additional heat-exchange apparatus – to the outlet from the turbine. This cycle is carried out as follows. In the vapor generator the strong solution heats up and thus separates into the flows of the refrigerant vapor and weak solution.

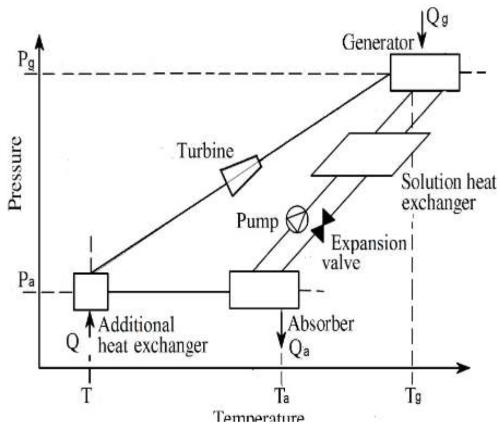

Fig. 5. Basic model of the absorption heat engine

Further on the weak solution from the vapor generator is fed into the absorber and its parameters (temperature and pressure) are adjusted to the desired values (T_a and $P_a = P_e$) by means of a heat exchanger and an expansion valve. Another flow, the vapor flow of refrigerant, enters first the turbine where it is expanded with the production of work, and the spent vapor after the turbine is fed into the absorber where it is taken up by the weak solution to yield the strong solution. In its turn the strong solution is supplied by a pump to the vapor generator with its intermediate heating in the recuperative heat exchanger of solutions. Alongside with that, the vapor of the refrigerant at the outlet from the turbine has a lower temperature T_e than the absorption temperature $T_a > T_e$ and may be used for cooling the external objects by means of the additional heat-exchange apparatus.

In such a comparison it was assumed that the performance of the turbine η_t and the heat-exchange apparatuses η_{ex} in the AHE cycles, the same as in the Carnot cycles, is equal to one, and the quantity of work consumed by the circulation pump is neglected because of its smallness.

To choose the properties of the working fluids (refrigerants, absorbents and solutions) one has used both the reference data [15,16] and the known investigations of absorption refrigerators [17–20].

With allowance made for these assumptions, the performance η_a of the AHE cycle is expressed by the Eq. (4)

$$\eta_a = w_a / q_g \tag{4}$$

displaying the degree of conversion of heat q_g consumed in the vapor generator into work w_a. The value of specific work w_a is determined by Eq. (5)

$$w_a = h_g - h_{out} \tag{5}$$

Where h_g and h_{out} – enthalpy of vapor of refrigerant at the inlet into the turbine and at the outlet from it.

The specific amount of heat q_g consumed in the vapor generator is determined by Eq. (6)

$$q_g = h_g - h_s + f(h_s - h_{in}), \tag{6}$$

where h_s and h_{in} – enthalpy of solution at the outlet from the vapor generator and at the inlet into it correspondingly, and f – the circulation ratio of solution.

In its turn, the coefficient of performance of the reversible Carnot cycle η_c corresponding to the temperatures of the hot T_g and cold T_a heat sources is defined by the Eq. (7)

$$\eta_c = \left(T_g - T_a\right)/T_g\ . \tag{7}$$

The results of the comparative assessment of the performance of the single-effect AHE cycles η_a and of the reversible Carnot cycle η_c are listed in Table 2.

The results of such an assessment illustrate that similarly with the cycles of absorption refrigerators noted above, the AHE cycles can have a greater performance than the maximum value of this index allowable today in the corresponding Carnot cycles too.

Table 2. Characteristic indices of an AHE cycle

Name of the index	Value of the index	
Working fluid	**CH_3OH-LiBr**	**NH_3-$LiNO_3$**
Solution generator inlet/outlet:		
temperature, ℃	95/115,9	108/132
pressure, kPa	100/100	1500/1500
refrigerant concentration, mass. %	53/45	40/32
Solution absorber inlet/outlet:		
temperature, ℃	21.1/41.8	24/50
pressure, kPa	1.58/1.58	116/116
refrigerant concentration, mass. %	45/53	32/40
Vapor turbine inlet/outlet:		
temperature, ℃	105/–19.3	120/–30
pressure, kPa	100/1.58	1500/116
enthalpy, kJ/kg	1326.4/978	1720/1368
refrigerant concentration, mass. %	100	100
Circulation ratio	6.87	8.5
Heat load of vapor generator, kJ/kg	1284.2	1546
Work of turbine, kJ/kg	348.4	352
Efficiency relative to Carnot cycle η_a/η_c, more than	1.2	1.08

The difference in the performance of these cycles becomes all the more evident in an additional convergence of the conditions of comparison of the AHE and Carnot cycles.

To this end one should assume that the expansion of the working fluid in the Carnot cycle occurs not at constant temperature of the hot heat source ($T_g = const$), as is usually adopted, but in a continuous lowering of its temperature during the process of expansion, just as happens in the AHE cycles.

Such a Carnot cycle is commonly designated the equivalent one, and its mean temperature T_m of the isothermal expansion of the working fluid is given by Eq. (8)

$$T_m = \left(T_g - T_a\right)/ln\left(T_g/T_a\right). \quad (8)$$

In so doing, the maximum possible work w_{cm} of such a Carnot cycle being equal to the specific work of expansion of the working fluid $w_a = w_{cm}$ in the adiabatic process is defined by Eq. (9)

$$w_{ad} = w_{cm} = RT_m \ln\left(P_g/P_a\right) \quad (9)$$

where $R-gas\ constant$, P_g and P_a – correspondingly initial and final pressure of the working fluid in its adiabatic expansion at temperature difference $\left(T_g - T_a\right)$.

The coefficient of performance of such a cycle η_{cm} is generally determined according to a well-known expression which uses the mean temperature T_m of heating and expansion of the working fluid

$$\eta_{cm} = (T_m - T_a)/T_m\ . \quad (10)$$

In such a comparison the relative performance of the AHE cycles under consideration η_a/η_{cm} exceeds the performance of the corresponding equivalent Carnot cycle by a factor larger than 2.2 for the CH_3OH-LiBr solution and nearly 1.9 for NH_3-$LiNO_3$ solution.

4. DISCUSSION

The above noted peculiarities of the cycles (models) of AHTs (absorption heat transformers) do not quite correlate with the commonly adopted assumptions of the equilibrium thermodynamics. Specifically, they point to a possibility of improving the performance of such cycles beyond the limits earlier confined by a relative temperature difference of external heat sources, as it is usually suggested.

However, the possibility of a deviation from this condition is quite allowable in the non-equilibrium energy systems [14], with the internal energy sources being available therein too. In this case the behavior of such systems can differ significantly from the well-known notions of the classical method.

In particular, it becomes therewith necessary to take into account the dependence of entropy not only on the thermal interactions, as was suggested usually, but also on the concentration of particles [21]. Besides, as was shown in [14], the efficiency of non-equilibrium cycles is determined rather not by the temperatures of external heat sources but by the relative temperature difference of the working fluid at the upper and lower temperature levels of the cycle.

With this in mind, the use of such thermodynamic peculiarities of absorption technologies opens up fresh opportunities for further enhancement of the efficiency of conversion of low-grade heat into electric power. Moreover, at the present time favorable technical prerequisites for the realization of these opportunities are already available as it follows from the latest reviews of the literature in the field of AHTs, represented, for example, in articles [22-24].

The energetic effects expected in further implementation of such opportunities can be rather essential because in comparison with the analogous ORC and Kalina technologies finding at the present time wide use for similar purposes their useful temperature range can be increased by a factor of nearly 1.5 to 2.

5. CONCLUSIONS

The examination of the thermodynamic models of absorption cycles from the standpoint of non-equilibrium thermodynamics allowing substantial deviations from the second law of thermodynamics to a greater extent than earlier corresponds to the current practice, as well as opens up fresh opportunities for further enhancement of the efficiency of production of electric power, heat and cold when using low-grade heat sources.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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