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High temperature electrochemical heat pump using water gas shift reaction. Part I: Theoretical considerations

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Abstract

A new electrochemical heat pump using a combination of an electrolytic reaction at lower temperature to absorb low grade thermal energy and a thermochemical reaction at higher temperature to produce more efficient thermal energy is proposed. At a lower temperature, an endothermic reaction which cannot occur thermochemically proceeds with electrolysis. At a higher temperature, an exothermic reaction which is the reverse of the electrolysis reaction occurs thermochemically to produce high grade thermal energy. The water gas shift reaction, $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, in molten carbonate is one possible candidate for the new electrochemical heat pump and can lead to an increase in the temperature of the thermal energy from 1100 to 1200 K. A heat pump system using the shift reaction is also considered theoretically.

1. Introduction

A heat pump system absorbs low grade thermal energy and produces high grade thermal energy that can be used more efficiently. Among heat pump systems, a chemical heat pump has the following advantages [1, 2]: (i) easy storage and transport, (ii) high density of heat storage. A conventional chemical heat pump, however, has the following disadvantages: (i) the system is complicated due to the coupling of two or more thermochemical reactions; (ii) The reaction systems which are applicable to the present chemical heat pump are restricted to solid–gas or liquid–gas reactions; and (iii) The existing systems are difficult to apply to industrial high temperature waste heat. The application of electrical energy has the potential to ameliorate the first two disadvantages. As the result of the application of electrical energy, the system, which is called an 'electrochemical heat pump', becomes simple and can constitute a single redox reaction. Thus, a greater variety of reactions that cannot occur thermochemically can be applied in the system. Furthermore, when a molten salt is used as an electrolyte, the system is expected to have a high coefficient of performance due to the high temperature operation.

In this paper, we propose a new concept for an electrochemical heat pump in which the electrical energy used in electrolysis is minimized.

The water gas shift reaction, $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$, is one candidate reaction for the new electrochemical heat pump system, where the electrolytic reactions, the reduction of CO_2 to CO at the cathode and the oxidation of H_2 to H_2O at the anode, proceed at lower temperature.

2. A new concept for an electrochemical heat pump

The new electrochemical heat pump uses the combination of an electrolytic reaction at lower temperature to absorb low grade thermal energy and a thermochemical reaction at higher temperature to produce high grade thermal energy. At a lower temperature, an endothermic reaction which cannot occur thermochemically proceeds by electrical energy input to absorb the lower temperature thermal energy, while at higher temperature, the reverse exothermic reaction occurs thermochemically to produce the higher temperature thermal energy. In total, this system absorbs low grade thermal energy by applying electrical energy and produces high grade thermal energy, as shown in Figure 1.

Kreysa reported an electrochemical heat pump consisting of two identical electrochemical cells operating at different temperatures in opposite directions [3, 4]. The difference between these two electrochemical heat pumps is the manner of thermal energy production at higher temperature. Our electrochemical heat pump produces thermal energy due to changes in enthalpy using a thermochemical reaction, whereas Kreysa's

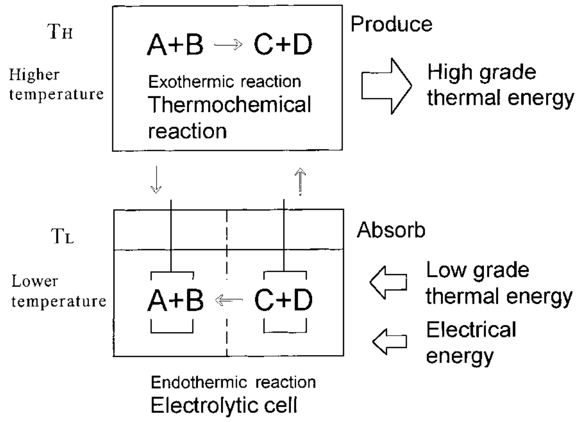

Fig. 1. Principle of a new electrochemical heat pump.

device produces thermal energy due to changes in entropy using galvanic cells.

3. Thermodynamic consideration of a new electrochemical heat pump

3.1. *Selection of the chemical reaction applied to the new electrochemical heat pump*

The objective here is to discuss the conditions of the chemical reactions applied to the new electrochemical heat pump and to investigate the candidates. The reaction should be redox, because the system involves electrolysis to produce the endothermic reaction.

To obtain high efficiency using the heat pump, the ΔG (Gibbs energy change) of the electrolytic reaction should be far smaller than the ΔH (enthalpy change) of the thermochemical reaction. When the equilibrium of the reaction is far shifted in favour of either the reactants or the products (i.e., the standard Gibbs energy change of reaction $\Delta G^\circ \ll 0$ or $\Delta G^\circ \gg 0$), the theoretical voltage for the electrolysis becomes large. Therefore, it is desirable to choose a reaction system which has a reverse temperature T^* (where $\Delta G^\circ = 0$) in the neighbourhood of the operating temperature.

From a kinetic point of view, the reaction should occur rapidly in both electrolysis and thermochemical reaction processes. That is to say, the thermochemical reaction can occur fluently using appropriate catalysts and the overvoltage of the electrolysis is small. Furthermore, the working substances should desirably be fluids under practical conditions of storage and transport. In particular, gases are favourable substances due to their easy transport.

Table 1. Several gas redox reactions which have the reverse temperature in the neighbourhood of the industrial high temperature waste heat

Reaction	Reverse temp./K	ΔH°_{298} /kJ mol^{-1}	ΔS°_{298} /JK^{-1} mol^{-1}
$CO+3\,H_2 \rightleftharpoons CH_4+H_2O$	890	−205.69	−214.5
$2CO+2H_2 \rightleftharpoons CH_4+CO_2$	912	−246.85	−256.58
$4\,NO+3\,H_2 \rightleftharpoons 2\,NH_3+2\,NO_2$	990	−386.86	−370.06
$SO_2+1/2O_2 \rightleftharpoons SO_3$	1051	−98.89	−94.03
$CO+H_2O \rightleftharpoons CO_2+H_2$	1095	−41.16	−42.08

ΔH°_{298} standard enthalpy change at 298 K
ΔS°_{298} standard entropy change at 298 K

There are several gas redox reactions which have the reverse temperature in the neighbourhood of the industrial high temperature waste heat, as shown in Table 1. Among these candidates, the most highly reactive one should be selected for application to the new electrochemical heat pump. The water gas shift reaction (1), as is well-known, may proceed to the right thermochemically with heat release using an appropriate catalyst such as Fe_2O_3/Cr_2O_3 [5].

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \tag{1}$$

The kinetic data for other reactions in Table 1 are hardly obtained, especially for electrolysis.

When molten carbonate is used as an electrolyte, the reverse electrolysis reaction of the water gas shift reaction can be divided into the following two half-cell reactions.

$$2\,CO_2\,(g) + 2\,e^- \rightarrow CO\,(g) + CO_3^{2-}\,(l) \tag{2}$$

$$H_2\,(g) + CO_3^{2-}\,(l) \rightarrow H_2O\,(g) + CO_2\,(g) + 2\,e^- \tag{3}$$

In electrolysis, the electrical energy input enables Reactions 2 and 3 to proceed to the right with heat absorption. The reaction of H_2 to H_2O in molten carbonate (Reaction 3) has been reported to proceed very easily as the anode reaction of a molten carbonate fuel cell [6, 7]. Therefore, the reduction of CO_2 to CO (Reaction 2) is considered to be the key reaction in the electrochemical heat pump using shift Reaction 1. This paper discusses the behaviour of the new high temperature electrochemical heat pump using the water gas shift reaction.

3.2. *Thermochemical diagram of the water gas shift reaction*

To consider the new high temperature electrochemical heat pump using the water gas shift reaction theoretically, the electrolysis and thermochemical reaction processes are treated as a closed system. The initial state of the closed system is assumed to be the state involving CO(g) 1 mol and H_2O(g) 1 mol. The extent of the reaction ξ, $d\xi = dn/v$, where dn is a change in moles and v is a stoichiometric number, is introduced. The total molarity in the closed system remains at 2 mol. When the reaction gases are assumed to behave ideally, the thermodynamic properties of the gases are

$$\mu_{CO} = \mu^\circ_{CO} + RT\,\ln((1-\xi)/2) \tag{4}$$

$$\mu_{H_2O} = \mu^{\circ}_{H_2O} + RT\ \ln((1-\xi)/2) \tag{5}$$

$$\mu_{CO_2} = \mu^{\circ}_{CO_2} + RT\ \ln(\xi/2) \tag{6}$$

$$\mu_{H_2} = \mu^{\circ}_{H_2} + RT\ \ln(\xi/2) \tag{7}$$

$$h_{CO} = h^{\circ}_{CO} \tag{8}$$

$$h_{H_2O} = h^{\circ}_{H_2O} \tag{9}$$

$$h_{CO_2} = h^{\circ}_{CO_2} \tag{10}$$

$$h_{H_2} = h^{\circ}_{H_2} \tag{11}$$

$$s_{CO} = s^{\circ}_{CO} - R\ \ln((1-\xi)/2) \tag{12}$$

$$s_{H_2O} = s^{\circ}_{H_2O} - R\ \ln((1-\xi)/2) \tag{13}$$

$$s_{CO_2} = s^{\circ}_{CO_2} - R\ \ln(\xi/2) \tag{14}$$

$$s_{H_2} = s^{\circ}_{H_2} - R\ \ln(\xi/2) \tag{15}$$

where, for substance A, μ_A is the chemical potential, h_A is the partial molar enthalpy, s_A is the partial molar entropy, R is the gas constant, T is the absolute temperature and the superscript (°) represents the standard state.

From the thermodynamic relation, the Gibbs energy G, the enthalpy H and the entropy S of the closed system are

$$G = \mu_{CO} \cdot n_{CO} + \mu_{H_2O} \cdot n_{H_2O} + \mu_{CO_2} \cdot n_{CO_2} + \mu_{H_2} \cdot n_{H_2} \tag{16}$$

$$H = h_{CO} \cdot n_{CO} + h_{H_2O} \cdot n_{H_2O} + h_{CO_2} \cdot n_{CO_2} + h_{H_2} \cdot n_{H_2} \tag{17}$$

$$S = s_{CO} \cdot n_{CO} + s_{H_2O} \cdot n_{H_2O} + s_{CO_2} \cdot n_{CO_2} + s_{H_2} \cdot n_{H_2} \tag{18}$$

where n_A is the number of moles of substance A and $n_{CO} = n_{H_2O} = 1 - \xi$, $n_{CO_2} = n_{H_2} = \xi$ in the present case.

Equations 16–18 indicate that each of these thermodynamic properties is a sole function of ξ at a certain temperature and pressure. Although the absolute values of G and H cannot be obtained, the changes in these function are necessary to analyse the performance of the electrochemical heat pump. Therefore, $G - (\mu^{\circ}_{CO} + \mu^{\circ}_{H_2O}), H - (h^{\circ}_{CO} + h^{\circ}_{H_2O})$, and $T\{S - (s^{\circ}_{CO} + s^{\circ}_{H_2O})\}$ which can be calculated from thermal data [8] are abbreviated as G, H and $T \cdot S$, and the dependence of these functions on ξ at $T = 1200$ K is shown in Figure 2.

Irreversible chemical processes occurring at a certain temperature and pressure decrease the Gibbs energy of the closed system. The equilibrium state of the closed system represents the minimum point of the Gibbs energy that is shown in the curve of Figure 2. At this point, the extent of the reaction, the Gibbs energy, the enthalpy and the entropy have the values, ξ_e, G_e, H_e and S_e, respectively.

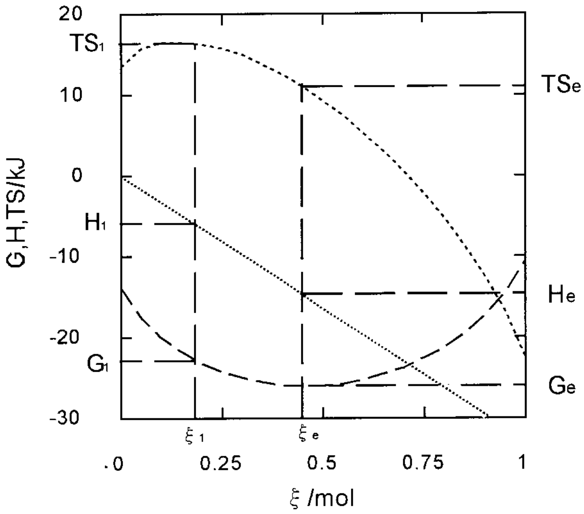

Fig. 2. Dependence of G, H and $T \times S$ on ξ at $T = 1200$ K. Key: (G) – – –; (H) ······ and ($T \times S$) - - -.

Let us consider the nonequilibrium state of the extent of the reaction ξ_1. The Gibbs energy, the enthalpy, the entropy at ξ_1 are expressed as G_1, H_1 and S_1, respectively. The Gibbs energy decreases from G_1 to G_e when the reaction occurs from ξ_1 to ξ_e thermochemically. At the same time, the heat, $(H_1 - H_e)$, is released. When the extent of the reaction is changed inversely from ξ_e to ξ_1, external work such as electrical energy should be provided to the system to increase the Gibbs energy from G_e to G_1. The absorbed heat accompanying the change is $T(S_1 - S_e)$, which is called reversible heat. The behaviour of the new electrochemical heat pump is considered using this diagram.

3.3. *Behaviour of new electrochemical heat pump*

Figure 3 shows the two diagrams at different temperature, that is, $T_H = 1200$ K (upper) and $T_L = 1100$ K (lower), with adjustment of each X axis. The extent of the reaction corresponding to equilibrium at higher temperature is expressed as ξ_e. The change in the extent of the reaction due to the electrolysis at T_L is depicted as $\Delta\xi$ and $\xi_e - \Delta\xi$ is expressed as ξ_1. $\Delta\xi$ is also equal to the change due to the thermochemical reaction at T_H. Here, the subscripts H and L designate higher and lower temperatures, respectively.

In the electrochemical heat pump, the water gas shift reaction [1] proceeds from right to left by the electrolysis. The theoretical voltage of the electrolysis U_{th} is given by the partial derivative $(\partial G/\partial \xi)_{T,P}$ and depends on the gas composition of the system.

$$U_{th} = -\frac{1}{2F}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} \tag{19}$$

where F is the Faradaic constant. The electrolytic cell takes up heat $(T_L S_{1,L} - T_L S_{e,L})$ reversibly from the lower

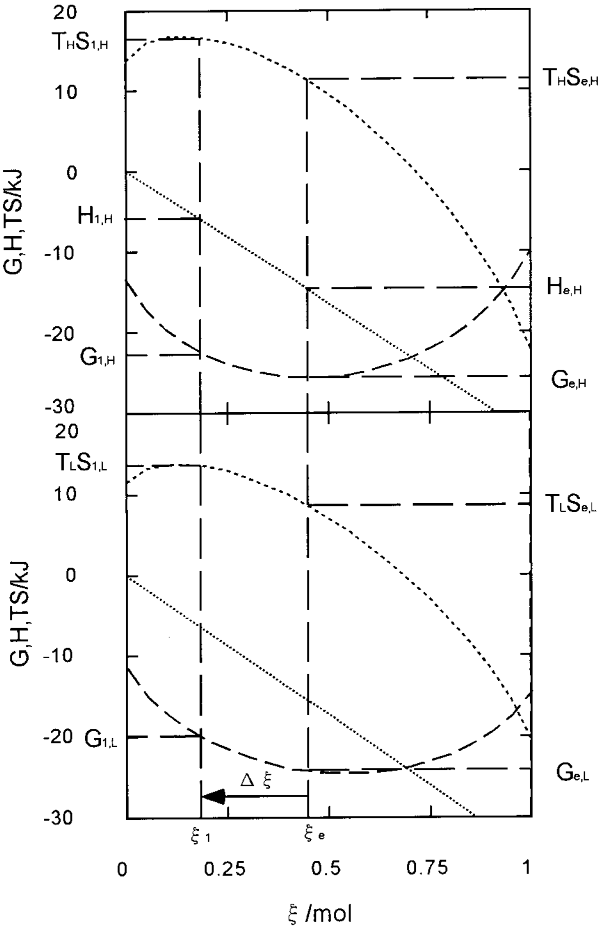

Fig. 3. Behaviour of a new electrochemical heat pump. Temperature: T_H = 1200 K (upper); T_L = 1100 K (lower). Key: (G) – – –; (H) ······ and ($T \times S$) - - -.

temperature reservoir by the electrical energy input, ($G_{1,L} - G_{e,L}$). The reaction system is then removed to higher temperature, fixing the gas composition represented by ξ_1. A spontaneous reaction occurs thermochemically until ξ_e at which state the reaction is in equilibrium at T_H with heat release ($H_{1,H} - H_{e,H}$).

The coefficient of performance (COP) of a heat pump is defined as the ratio of the heat output Q_H at T_H to the electrical energy input W_e at T_L. In the case of the new electrochemical heat pump, COP is expressed as

$$\mathrm{COP} = \frac{Q_H}{W_e} = \frac{H_{1,H} - H_{e,H}}{G_{1,L} - G_{e,L}} \tag{20}$$

Both W_e and COP are functions of $\Delta\xi$, T_H and T_L, and Q_H is a function of $\Delta\xi$ and T_H. Figure 4 shows the dependence of Q_H and W_e on $\Delta\xi$ when T_H and T_L are fixed at 1200 K and 1100 K, respectively. Q_H is proportional to $\Delta\xi$, because the enthalpy H has a linear relation with ξ. Whereas, W_e is far from linearity with $\Delta\xi$, as shown in Figure 4. Consequently, as $\Delta\xi$ increases, the value of W_e approaches Q_H. This means that the COP decreases rapidly with increasing $\Delta\xi$ and approaches unity. Figure 5 represents the dependence of the COP on $\Delta\xi$ at T_L = 1150, 1100 and 1050 K, fixing T_H at 1200 K. In any case, COP decreases rapidly with increasing $\Delta\xi$ and finally becomes unity.

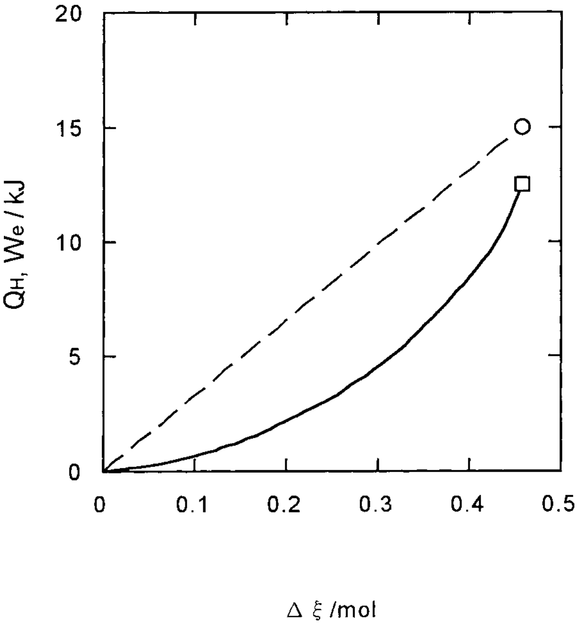

Fig. 4. Dependence of Q_H and W_e on $\Delta\xi$. T_H = 1200 K; T_L = 1100 K. Key: (□) W_e and (○) Q_H.

3.4. *Consideration of entropy production due to internal irreversibility*

Let us consider the reason why the COP decreases with increasing $\Delta\xi$ by introducing the concept of irreversibility. When the first and second law equations are applied to a heat pump cycle, they give

$$Q_H = Q_L + W_e \tag{21}$$

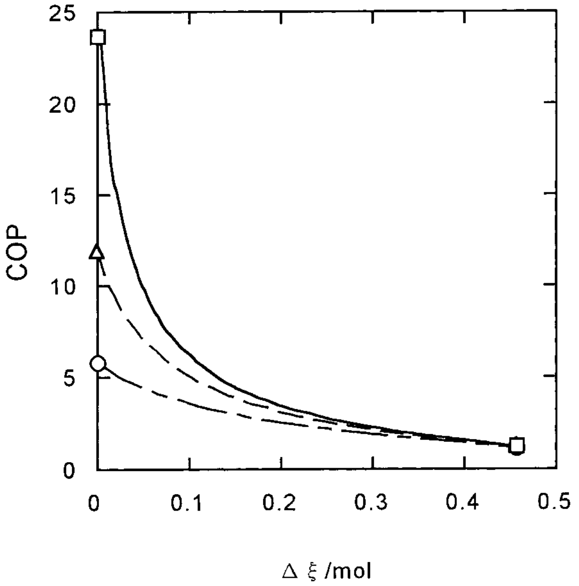

Fig. 5. Dependence of COP on $\Delta\xi$ at T_L = 1150 K (———); 1100 K (– – –) and 1000 K (— - -). T_H = 1200 K.

$$Q_H/T_H = Q_L/T_L + \sigma \quad (22)$$

where Q_L is the absorbed heat at T_L and σ is the quantity of the entropy production due to the internal irreversibility. In Equation 22, the second term on the right side, σ, is always positive by nature and would become zero only when all the processes in the cycle are internally reversible. Rearranging Equations 21 and 22, Q_H, W_e, and COP including the term σ are expressed as

$$Q_H = T_H/T_L \times Q_L + T_H\sigma \quad (23)$$

$$W_e = (T_H - T_L)/T_L \times Q_L + T_H\sigma \quad (24)$$

$$\mathrm{COP} = T_H/(T_H - T_L) - T_H T_L/(T_H - T_L) \times \sigma/W_e \quad (25)$$

It is found that both Q_H and W_e increase with increasing σ. The essential irreversibility in the new electrochemical heat pump is in the thermochemical reaction process at higher temperature. When the reaction occurs thermochemically, the change in the Gibbs energy, which can be utilized as available work, transforms unavailable energy (i.e., heat). Equation 24 indicates that more electrical energy input is necessary as the irreversibility increases. According to Equation 25, the COP decreases with increasing σ/W_e. To obtain a high COP value, the reaction included in the electrochemical heat pump should proceed reversibly.

It is possible to transport the reaction substances continuously, if all the reactants are gases or liquids. The water gas shift reaction is composed of gaseous species. When the amount of each species is very large compared to the extent of the reaction, the composition of the system can be held near the equilibrium. The products of the electrolysis, CO and H_2O, can be removed continuously to the higher temperature reactor and allowed to react thermochemically with heat release until the reaction reaches equilibrium. The products, CO_2 and H_2, are then returned to the electrolytic cell at lower temperature. As a whole, the heat pump is operated in a closed system; it is possible to circulate the reaction substances continuously between the two reactors. A large amount of the reaction substances makes $\Delta\xi$ very small. Due to the continuous transport of the reaction substances, the heat pump reactions can be operated near ξ_e at any time. For the process in which $\Delta\xi$ is very small, Equation 25 results in the reciprocal Carnot factor, which has the maximum value under the given T_H and T_L conditions.

$$\mathrm{COP} = \mathrm{T_H}/(\mathrm{T_H} - \mathrm{T_L}) \quad (26)$$

3.5. *Dependence of T_H and ΔT on COP with continuous transportation of reaction substances*

Figure 6 shows the dependence of the COP on temperature difference between the higher and lower thermal reservoirs with continuous transport of the reaction substances at several T_H. It is apparent from this Figure that the COP increases with increasing T_H and with decreasing ΔT.

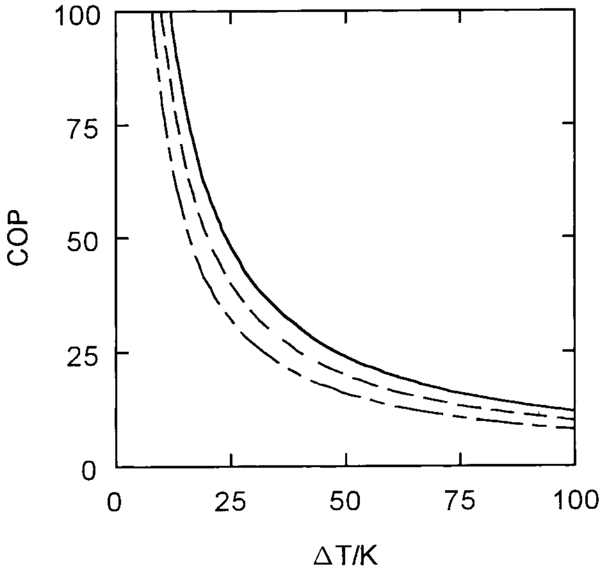

Fig. 6. Dependence of COP on temperature difference between higher and lower thermal reservoirs with continuous transportation of reaction substances. Key for T_H: (———) 1200 K; (– – –) 1000 K and (– – – –) 800 K.

4. Conclusions

- (i) A new electrochemical heat pump using a combination of an electrolytic reaction at lower temperature to absorb low grade thermal energy and a thermochemical reaction at higher temperature to produce more efficient thermal energy was proposed.
- (ii) The behaviour of the new electrochemical heat pump using the water gas shift reaction was described using a thermochemical diagram.
- (iii) The absorbed heat, the electric energy input, and the coefficient of performance of the new electrochemical heat pump were calculated from the thermal data. The relationship between these values and the irreversibility was derived.
- (iv) It was shown that the COP of the electrochemical heat pump with the continuous transport of the reaction substances would approach the value of the inverse Carnot factor.

The reactivity of the redox reaction applied to the electrochemical heat pump should be analysed experimentally. In the case of the water gas shift reaction, it is necessary to examine the reactivity of the reduction of CO_2 to CO.

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