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Thermodynamic properties of metal hydrides for a novel heat pump configuration

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Abstract

A novel heat-driven metal hydride heat pump configuration is described in which the enthalpy of formation of the cooling (or refrigeration) hydride contributes to the heat required to regenerate that hydride. The major advantage of this configuration is that the values of the theoretical coefficients of performance are considerably higher than those of a conventional hydride heat pump. However, the disadvantage of this concept is that heat capacity losses are greater, because higher temperatures are required for regeneration than in the conventional system. The required thermodynamic properties of the hydride pairs necessary to obtain low refrigeration temperatures, low regeneration temperatures, and high coefficients of performance are considered. Several hydride pairs are discussed, and a comparison is made to a conventional heat pump.

Keywords: Thermodynamic properties; Metal hydrides; Heat pump

1. Introduction

The operation of a conventional heat-driven metal hydride heat pump for cooling is illustrated in Fig. 1. The system consists of two different hydrides; a refrigeration hydride, M_2H_y, and a regeneration hydride, M_1H_x. As hydrogen flows from points A to B, the refrigeration hydride M_2H_y cools to the temperature T_c while the regeneration hydride is held at ambient temperature, T_m.

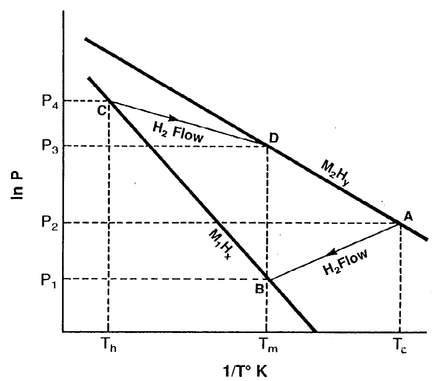

Fig. 1. Operation of a conventional metal hydride heat pump in the cooling mode.

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The refrigeration hydride can be regenerated by allowing it to return to ambient temperature and heating the regeneration hydride to a higher temperature, T_h, thus permitting hydrogen flow from point C to D.

The operating pressures are determined by the van't Hoff relationship:

$$R \ln P = (\Delta H/T) - \Delta S \quad (1)$$

where ΔH and ΔS are the enthalpies and entropies of formation of the hydrides, respectively. In order to maintain hydrogen flow during cooling, the pressure of the refrigeration hydride must always be higher than that of the regeneration hydride. Since ΔS values of different hydrides generally do not vary greatly, the hydrogen pressure of a hydride is usually determined by the ΔH values. The heats of formation of stable metallic hydrides are always negative. Therefore, according to Eq. (1), the lower the absolute value of ΔH, the higher the hydrogen pressure.

The theoretical coefficient of performance, $(COP)_t$ of the hydride heat pump in Fig. 1, is given by:

$$(COP)_t = \Delta H_c/\Delta H_h \quad (2)$$

where ΔH_c and ΔH_h are the enthalpies of formation of the refrigeration and regeneration hydride, respectively. Since the pressure of the refrigeration hydride must be higher than that of the regeneration hydride, $|\Delta H_c| < |\Delta H_h|$. Therefore, the $(COP)_t$ of the hydride heat pump shown in Fig. 1 is almost always less than unity (unless there is a large difference in ΔS values [1]).

2. Crossed van't Hoff lines concept

In order to obtain values of $(COP)_t$ greater than unity, Stein and Redding [2] proposed the configuration shown in Fig. 2, in which the van't Hoff curves cross. Since the temperature at point D becomes higher than that at point C during regeneration, the heat of formation of the refrigeration hydride can be recovered and transferred to the regeneration hydride, via a one-directional heat pipe, while hydrogen flow from point C to point D is still maintained. Thus, the heat of absorption of the refrigeration hydride, ΔH_c, contributes to the heat required to drive the regeneration process.

The theoretical *COP* for this process then becomes:

$$(COP)_t = \Delta H_c / (\Delta H_h - \Delta H_c) \quad (3)$$

which results in higher values of $(COP)_t$; usually greater than unity. For example, for the case in which $LaNi_5$ is used as the refrigeration hydride ($\Delta H_c = -31.0$ kJ mole H_2^{-1}) and $V_{0.86}Ti_{0.09}Fe_{0.05}$ as the regeneration hydride

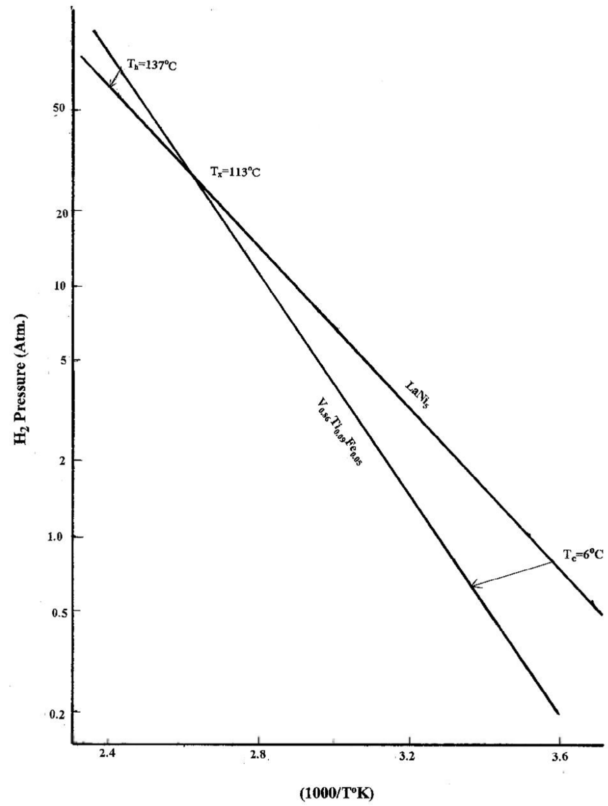

Fig. 3. Example of a crossed van't Hoff lines metal hydride heat pump with $LaNi_5$as the refrigerant hydride and a V–Ti–Fe alloy as theregenerative hydride.

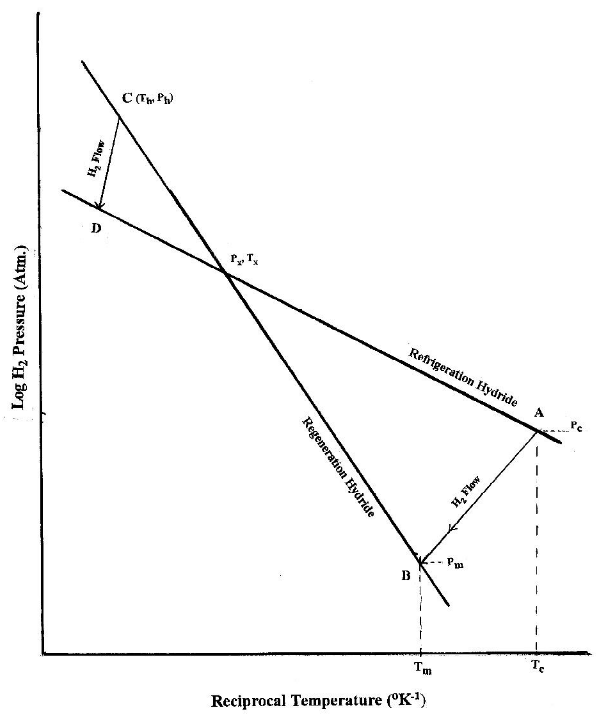

Fig. 2. Operation of a metal hydride heat pump based on crossed van't Hoff lines.

($\Delta H_h = -43.2$ kJ mole H_2^{-1}) as illustrated in Fig. 3:

$$(COP)_t = 31.0/(43.2 - 31.0) = 2.5.$$

If the same hydrides were used in a conventional hydride heat pump:

$$(COP)_t = 31.0/43.2 = 0.72.$$

In order to facilitate a search for appropriate hydride pairs for the configuration in Fig. 2, Eqs. (4)–(7) were derived, utilizing the fact that at the crossover temperature, T_x, the hydrogen pressures of the refrigeration hydride and regeneration hydride are equal (P_x).

For the refrigeration hydride:

$$\Delta H_c = T_c T_x [R \ln(P_x/P_c)]/(T_c - T_x) \quad (4)$$

$$\Delta S_c = R(T_x \ln P_x - T_c \ln P_c)/(T_c - T_x) \quad (5)$$

and for the regeneration hydride:

$$\Delta H_h = T_m T_x [R \ln(P_x/P_c)]/(T_m - T_x) \quad (6)$$

$$\Delta S_h = R(T_x \ln P_x - T_m \ln P_c)/(T_m - T_x). \quad (7)$$

In deriving Eqs. (6) and (7), the assumption was made

Table 1

Hydride pairs Refrig./regen.	$[\Delta H]$ (KJ mole H_2^{-1})	$[\Delta S]$ (J mole H_2^{-1})	$(COP)_t$	T_c (°C)	P_x (atm)	T_x (°C)	T_h (°C)	Refs.
$LaNi_5$/	31.0	109						
$V_{0.855}Ti_{0.095}Fe_{0.05}$	43.2	140.6	2.5	5	28	113	137	[3,4]
$Fe_{0.9}Mn_{0.1}Ti$/	26.6	99.2						
$V_{0.846}Ti_{0.104}Fe_{0.05}$	42.9	148.5	1.6	14	9	58	71	[5,6]
$MmNi_{3.98}Fe_{1.04}$/	27.3	105.6						
$V_{0.846}Ti_{0.104}Fe_{0.05}$	42.9	148.5	1.8	2	40	91	107	[7,6]
$MmNi_{3.98}Fe_{0.85}$/	25.1	104.6						
$VCr_{0.05}$	37.4	139.3	2.0	10	56	80	101	[8,9]

that $P_c = P_m$. However, these equations were useful in identifying hydride pairs which may be appropriate for the crossed van't Hoff lines concept. For any possible refrigeration hydride (i.e. known values of ΔH_c and ΔS_c) these equations were used in a spreadsheet analysis program to suggest values of ΔH_h and ΔS_h for various values of P_x(or T_x). T_m was taken as room temperature, 298°K.

For each possible hydride pair, T_c and T_x can be calculated from the following equations (which are each derived from the van't Hoff relationships for each hydride):

$$T_c = (T_m \Delta H_c)/[\Delta H_h - T_m(\Delta S_h - \Delta S_c) - K] \quad (8)$$

when ΔH_c, ΔH_h, ΔS_c and ΔS_h are absolute values, and K is a term arising from the fact that P_c (in Fig. 2) must be higher than P_m (i.e. if $P_c = \alpha P_m$, $K = RT_m \ln\alpha$)

$$T_x = (\Delta H_h - \Delta H_c)/(\Delta S_h - \Delta S_c). \quad (9)$$

In order to maintain hydrogen flow from point A to point B (in Fig. 2) it was assumed that P_c would be 25% higher than P_m, i.e., $\alpha = 1.25$ and K in Eq. (8) then becomes 533.

Eqs. (4)–(7) were applied to many different hydride pairs. Some of the more interesting hydride pairs are shown in Table 1 along with T_c and T_x values calculated from Eqs. (8) and (9). The crossed van't Hoff lines for the first hydride pair in Table 1 is shown in Fig. 3. The T_c values in Table 1 are not low enough to permit use in refrigeration systems, which would require a value of about −20°C. However, they may be low enough to be used for air conditioning.

3. Disadvantage of the crossed van't Hoff lines concept

The major disadvantage of the crossed van't Hoff lines concept is the requirement of higher temperatures and pressures (than the conventional system) for regeneration. This may limit the use of some hydride systems because the slopes of the pressure plateaux (of the P–C–T isotherms) sometimes increase with temperature and the widths of the plateaux usually decrease, leading to decreased efficiency of the heat pump.

Also, higher regeneration temperatures have a deleterious affect on the COP values because of higher specific heat loss. When these are taken into account, the COP for the conventional heat pump (Eq. (2)) becomes (per mole of H_2):

$$COP = [\Delta H_c - m_1 C_1 (T_m - T_c)]/[\Delta H_h + m_2 C_2 (T_h - T_m)] \quad (10)$$

and Eq. (3) (the crossed van't Hoff lines heat pump) becomes:

$$COP = [\Delta H_c - m_1 C_1 (T_m - T_c)]/[\Delta H_h - \Delta H_c + (m_1 C_1 + m_2 C_2)(T'_h - T_m)] \quad (11)$$

where m_1 and C_1 are the number of moles and the specific heat of the refrigeration hydride and m_2 and C_2 are the corresponding values for the regeneration hydride. T_h and T'_h are the temperatures required to maintain hydrogen flow during regeneration.

Because of the contribution of the additional (m_1C_1) term in the denominator of Eq. (11), as well as the fact that $(T_h - T_m)$ is always greater in the crossed van't Hoff lines heat pump, the reduction of the theoretical COP will always be greater for the crossed van't Hoff lines concept. However, since the theoretical COP values are much higher than those of the conventional heat pump, the actual COP values may still be greater for the crossed van't Hoff lines heat pump. A comparison was made for the first hydride pair in Table 1, $LaNi_5/V_{0.865}Ti_{0.095}Fe_{0.05}$. C_1 was estimated from the data of Ohlendorf and Flotow [10] and C_2 from Bieganski and Stalinski [11]. Using Eqs. (10) and (11), the COP for the conventional system was reduced from 0.71 to 0.64, and the COP of the crossed van't Hoff lines system was reduced from 2.5 to 0.83. This latter value is still greater than that for the COP for the conventional heat pump.

4. Conclusion

Although no completely satisfactory hydride pair has been identified for use in the crossed van't Hoff lines concept, particularly for refrigeration, there is still a possibility that appropriate hydride pairs can be found, either from newly discovered hydrides or modification of existing hydrides by partial substitution of other metals. As for all applications of metal hydrides, high hydrogen contents, low hysteresis and plateau slopes, and stability to disproportionation are required. However, in order to identify hydrides with appropriate thermodynamic properties for the crossed van't Hoff lines concept, the following three requirements must be considered: high *COP*, low T_c, and low T_x values.

As can be seen from Eqs. (2), (8), (9), some of these requirements are mutually exclusive, e.g., high values of ΔH_c will lead to high values of *COP* and low values of T_x, but also to high values of T_c. Therefore trade-offs must be considered.

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