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Short communication

Chemical and adsorption heat pumps: Comments on the second law efficiency

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Abstract

The thermodynamic analysis of an ideal cycle of chemical and adsorption heat pumps was performed in order to compare two definitions of the cycle efficiency used in literature and estimate the maximal efficiency that can be reached for particular non-regenerative cycle. It was shown that the efficiency equal to the Carnot efficiency can be, in principle, obtained for a chemical heat pump that results from a monovariant equilibrium of a gas–solid reaction. This was confirmed for various chemical reactions between salts and ammonia (or water). For a divariant equilibrium in adsorption heat pump there is inevitable degradation of the efficiency due to the thermal entropy production caused by the external thermal coupling. Simple estimation of the efficiency reduction is suggested.

Keywords: Solid sorption; Chemical heat pump; Adsorption; Solid–gas reaction; COP; Second law efficiency; Cycle analysis; Ammonia; Water; Methanol

1. Introduction

For every heat pumping machine the maximal theoretical Coefficient of Performance (COP) is the Canot COP. It was examined in a number of works [1–4]. A simple chemical heat pump (CHP) operating between three thermostats (I, II and III) maintained at high (T_g), middle (T_c) and low (T_e) temperatures (Fig. 1) will be considered in this paper. The CHP transforms heat under two modes, namely, cooling and heating. Such a three temperature (3T) CHP consists of an evaporator E at temperature T_e, a condenser C at temperature T_c and an adsorber (reactor) A connected with the appropriate thermostats (Fig. 1). The adsorber switches from the thermostat at T_g (regeneration stage, $T_r = T_g$) to the thermostat at $T_a = T_c$ (adsorption stage, $T_a = T_c$). For an ideal 3T system (with zero thermal masses) the energy balance (the first law)

$$Q_c - Q_e - Q_r + Q_a = 0$$

and the entropy balance (the second law)

$$-\frac{Q_c}{T_c} + \frac{Q_e}{T_e} + \frac{Q_r}{T_g} - \frac{Q_a}{T_a} = \Delta S \geq 0 \tag{1}$$

can be written. If all the processes are completely reversible, the entropy generation is equal to zero $\Delta S = 0$. In this case the Carnot COP for cooling $\mathrm{COP}_c^c = Q_e/Q_r$ and heating $\mathrm{COP}_c^h = (Q_c + Q_a)/Q_r$ can be calculated. Indeed, after substitution $Q_c = Q_e + Q_r - Q_a$ and $T_a = T_c$ into (1), it is easy to obtain

$$Q_e\left(\frac{1}{T_e} - \frac{1}{T_c}\right) - Q_r\left(\frac{1}{T_c} - \frac{1}{T_g}\right) = 0,$$

which directly gives the Carnot COP for cooling

$$\mathrm{COP}_c^c = \frac{Q_e}{Q_r} = \frac{(1/T_c) - (1/T_g)}{(1/T_e) - (1/T_c)}. \tag{2}$$

The Carnot COP for heating is

$$\mathrm{COP_c}^{\mathrm{h}} = \frac{Q_c + Q_a}{Q_r} = \frac{Q_r + Q_e}{Q_r} = 1 + \mathrm{COP}_c^c = 1 + \frac{(1/T_c) - (1/T_g)}{(1/T_e) - (1/T_c)} = \frac{(1/T_e) - (1/T_g)}{(1/T_e) - (1/T_c)}. \tag{3}$$

On the other hand, the cooling COP could be defined as a ratio $\Delta H_e/\Delta H_r$, where ΔH_e is the enthalpy of *evaporation* and ΔH_r is the average enthalpy of sorption for adsorption heat pump (AHP) or of chemical reaction for chemical heat pump [1,5]

$$\mathrm{COP}^c = \frac{\Delta H_e}{\Delta H_r}. \tag{4}$$

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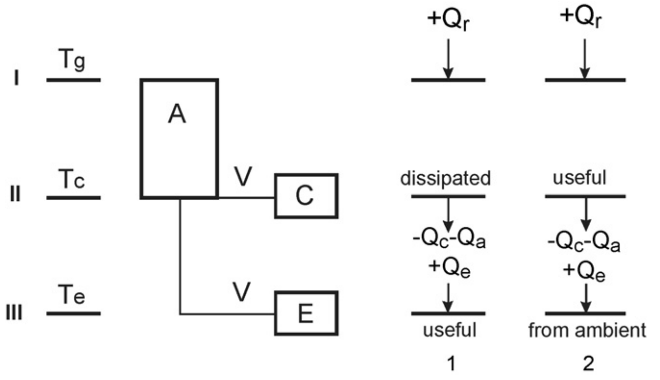

Fig. 1. Schematic of a 3T chemical (adsorption) heat pump working at cooling (1) and heating (2) modes. A: adsorber (reactor); C: condenser; E: evaporator; V: vapor.

In the same way for a heating cycle

$$\mathrm{COP}^{\mathrm{h}} = \frac{\Delta H_{\mathrm{c}} + \Delta H_{\mathrm{r}}}{\Delta H_{\mathrm{r}}} = 1 + \mathrm{COP}^{\mathrm{c}}. \quad (5)$$

In Eqs. (2) and (3) the maximal COP is evaluated by three temperatures only, and does not depend on the characteristics of the working pair in an explicit form. However, in Eqs. (4) and (5) the cycle temperatures are not presented, and the COP is determined by the enthalpy of condensation and sorption (reaction). In this work we discuss links between these two foregoing definitions of COP for the sorption thermal cycles based on chemical reaction and adsorption phenomena. The ratio $\eta = \mathrm{COP}/\mathrm{COP}_{\mathrm{c}}$ gives the second law efficiency of the CHP (AHP) cycle [1].

1.1. Thermodynamic analysis of a chemical heat pump

In a chemical heat pump the sorption/desorption of gas occurs due to a chemical gas–solid reaction

$$\mathrm{A}_{\mathrm{gas}} + \mathrm{B}_{\mathrm{sol}} \Leftrightarrow (\mathrm{AB})_{\mathrm{sol}}. \quad (6)$$

This system consists of three components (A, B and AB) in three phases ($\mathrm{A}_{\mathrm{gas}}$, $\mathrm{B}_{\mathrm{sol}}$ and $(\mathrm{AB})_{\mathrm{sol}}$). According to the Gibbs phase rule the number of degrees of freedom v for the system with k components, f phases and r linearly independent reactions could be calculated as $v = k + 2 - f - r$ [6]. Thus, the examined system is monovariant ($v = 3 + 2 - 3 - 1 = 1$). If one of the free parameters (for example, P) is fixed, the variance is zero and the transition (6) occurs at a certain temperature T_{r}.

At a gas pressure equal to the pressure in condenser P_{c} the decomposition of a compound AB occurs at temperature T_{r} while at a pressure equal to the pressure in evaporator P_{e} the compound AB forms at temperature T_{a} (Fig. 2a). The correspondence between temperature and pressure on the equilibrium state line and the liquid/gas curves could be described by the Clausius–Clapeyron Eq. (6):

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = -\frac{\Delta H_{\mathrm{r}}(T)}{RT^2}, \quad (7)$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = -\frac{\Delta H_{\mathrm{e}}(T)}{RT^2}. \quad (8)$$

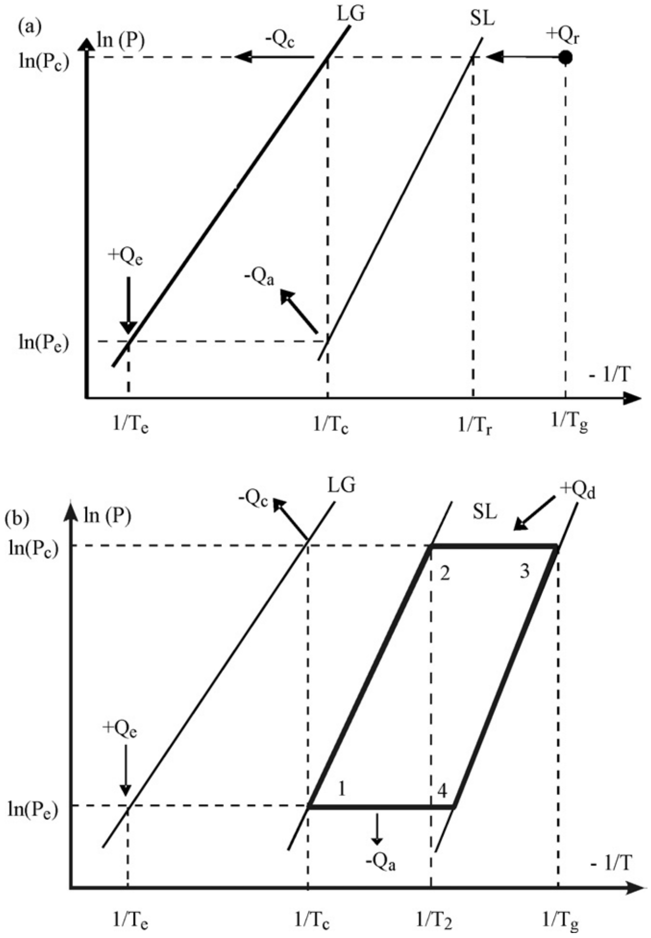

Fig. 2. Clapeyron diagrams of a 3T cycle of a chemical (a) and adsorption (b) heat pumps.

Neglecting the dependence $\Delta H_{\mathrm{e}}(T)$ and $\Delta H_{\mathrm{r}}(T)$, one can rewrite Eqs. (7) and (8) for the pressure ratio $P_{\mathrm{c}}/P_{\mathrm{e}}$ as

$$\begin{cases} R\,\ln\left(\dfrac{P_{\mathrm{c}}}{P_{\mathrm{e}}}\right) = \Delta H_{\mathrm{e}}\left(\dfrac{1}{T_{\mathrm{e}}} - \dfrac{1}{T_{\mathrm{c}}}\right), \\ R\,\ln\left(\dfrac{P_{\mathrm{c}}}{P_{\mathrm{e}}}\right) = \Delta H_{\mathrm{r}}\left(\dfrac{1}{T_{\mathrm{c}}} - \dfrac{1}{T_{\mathrm{r}}}\right). \end{cases}$$

Thus,

$$\Delta H_{\mathrm{e}}\left(\frac{1}{T_{\mathrm{e}}} - \frac{1}{T_{\mathrm{c}}}\right) = \Delta H_{\mathrm{r}}\left(\frac{1}{T_{\mathrm{c}}} - \frac{1}{T_{\mathrm{r}}}\right),$$

and for the $\mathrm{COP}^{\mathrm{c}}$

$$\mathrm{COP}^{\mathrm{c}} = \frac{\Delta H_{\mathrm{e}}}{\Delta H_{\mathrm{r}}} = \frac{(1/T_{\mathrm{c}}) - (1/T_{\mathrm{r}})}{(1/T_{\mathrm{e}}) - (1/T_{\mathrm{c}})}. \quad (9)$$

Comparing Eqs. (2) and (9), it is easy to find that $\mathrm{COP}^{\mathrm{c}} = \mathrm{COP}^{\mathrm{c}}_{\mathrm{c}}$ and $\eta = 1$, if $T_{\mathrm{g}} = T_{\mathrm{r}}$, i.e. if the temperature of the external heat source is equal to the temperature of AB decomposition. If $T_{\mathrm{g}} > T_{\mathrm{r}}$, then $\eta = [(1/T_{\mathrm{c}}) - (1/T_{\mathrm{r}})]/[(1/T_{\mathrm{c}}) - (1/T_{\mathrm{g}})] < 1$, and the decrease in η is caused by the entropy generation $\Delta S > 0$. For the entropy balance one can write at $T_{\mathrm{g}} = T_{\mathrm{r}}$

$$-\frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}} + \frac{Q_{\mathrm{e}}}{T_{\mathrm{e}}} + \frac{Q_{\mathrm{r}}}{T_{\mathrm{r}}} - \frac{Q_{\mathrm{a}}}{T_{\mathrm{c}}} = \Delta S = 0$$

and at $T_g > T_r$

$$-\frac{Q_c}{T_c}+\frac{Q_e}{T_e}+\frac{Q_r}{T_g}-\frac{Q_a}{T_c}=\Delta S>0,$$

hence, $\Delta S = Q_r((1/T_r) - (1/T_g))$. If $Q_r = \Delta H_r$ this value agrees with the entropy increase due to the irreversibility of the transfer of the reaction heat ΔH_r from the external heat source at temperature T_g to the reactor at temperature $T_r < T_g$.

Similarly, for the heating process

$$\mathrm{COP}^h = \frac{\Delta H_c + \Delta H_a}{\Delta H_r} = \frac{\Delta H_c}{\Delta H_r} + \frac{\Delta H_a}{\Delta H_r} = \frac{\Delta H_e}{\Delta H_r} + 1 = \frac{(1/T_e) - (1/T_r)}{(1/T_e) - (1/T_c)}. \qquad (10)$$

If $T_g > T_r$, then $\mathrm{COP}^h < \mathrm{COP}^h_c$ and $\eta = [(1/T_c) - (1/T_r)]/[(1/T_c) - (1/T_g)] < 1$ because of the aforesaid irreversibility of the heat transfer from the external heat source to the reactor.

Thus, for the CHP cycle based on the monovariant equilibrium the second law efficiency $\eta = 1$ for both cooling and heating processes, if the temperature of external heat source is equal to the temperature of the decomposition of complex AB. In this case the definition of the COP based on the cycle temperatures (Eq. (2)) and that based on the cycle enthalpies (Eq. (4)) are equivalent regardless of the chemical nature of working pair. This is due to the fact that under reversible operation these temperatures and enthalpies are linked by the Clausius–Clapeyron equation and cannot be arbitrarily chosen. Overspecification of Eq. (2) for reversible absorption heat pumps was discussed in [7].

For the 3T cooling cycle we calculated the values of COP using Eqs. (2) and (4) for several chemical reactions that are considered as promising for CHPs with ammonia and water as working fluids (Table 1). For fixed T_e the values of T_c and T_g, which corresponds to reversible operation of CHP, were obtained geometrically as shown on Fig. 2a. Values of ΔH_c and ΔH_r were taken from [8] for ammonia and from [9] for water. So calculated COPs appeared to be very close, and the difference between them was less than 2%. It demonstrates that for reversible CHP the two definitions of the COP (Eqs. (2) and (4)) are equivalent regardless of the chemical nature of working pair.

1.2. *Thermodynamic analysis of an adsorption heat pump*

Basic 3T cycle of an adsorption heat pump is displayed in Fig. 2b. The stages of the cycle are:

- 1–2 is an isosteric heating of the saturated adsorbent along the rich isoster from the initial temperature $T_1 = T_c$ to the minimal desorption temperature T_2.
- 2–3 is an isobaric desorption of the sorbate due to adsorbent heating from T_2 to the temperature $T_3 = T_g$ of an external heat source with subsequent condensation in the condenser.
- 3–4 is an isosteric cooling of the adsorbent along the weak isoster down to T_4.
- 4–1 is an isobaric adsorption that is driven by adsorbent cooling down to $T_1 = T_c$ and evaporation of sorbate in the evaporator.

The principal difference between CHP and AHP is that, in contrast to the "gas–solid" chemical reaction with monovariant equilibrium, the adsorbate–adsorbent equilibrium is bivariant. In this case the desorption process occurs not at a fixed temperature T_g but within a certain temperature interval from T_2 to $T_3 = T_g$. As a result, during isobaric desorption only at point 3 (at $T = T_g$) the temperature difference between the adsorber and the external heat source is zero. During adsorption phase, only at point 1 ($T = T_c$) there is no temperature difference between the adsorber and the external heat sink, and the entropy generation is zero. At any other temperature of the isobaric stages the entropy is generated due to the heat supply at $T_g - T > 0$ or the heat removal at $T - T_c > 0$, that inevitably reduces the cycle efficiency below the Carnot value calculated by Eq. (2).

Table 1
The maximal theoretical COP of various cooling cycles based on gas–solid reactions

Working pair	T_e	T_c	T_g	ΔH_c (kJ/mol)	ΔH_r (kJ/mol)	Carnot COP	$\Delta H_c/\Delta H_r$	Error (%)
NH_3–$BaCl_2$	−20.0	26.7	65.8	23.0	37.0	0.63	0.62	1.6
NH_3–$CaCl_2$	−20.0	45.6	100.9	23.0	40.2	0.57	0.57	0.0
NH_3–$SrCl_2$	−20.0	52.8	115.6	23.0	40.7	0.56	0.56	0.0
NH_3–$ZnCl_2$	−20.0	75.2	159.5	23.0	44.2	0.52	0.52	0.0
NH_3–$BaCl_2$	−5.0	39.9	76.4	23.0	37.0	0.62	0.62	0.0
NH_3–$CaCl_2$	−5.0	58.8	111.3	23.0	40.2	0.57	0.57	0.0
NH_3–$SrCl_2$	−5.0	66.3	126.4	23.0	40.7	0.57	0.56	1.8
NH_3–$ZnCl_2$	−5.0	89.7	171.3	23.0	44.2	0.52	0.52	0.0
NH_3–$BaCl_2$	+10.0	52.4	85.3	23.0	37.0	0.61	0.62	1.6
NH_3–$CaCl_2$	+10.0	71.7	120.4	23.0	40.2	0.57	0.57	0.0
NH_3–$SrCl_2$	+10.0	79.8	136.5	23.0	40.7	0.56	0.56	0.0
H_2O–$MgCl_2$[a]	20.0	70.8	120.3	42.8	59.9	0.72	0.73	1.4
H_2O–$MgCl_2$[b]	20.0	134.0	267.7	42.8	66.3	0.65	0.64	1.6
H_2O–MgO[c]	20.0	186.5	367.5	42.8	83.2	0.51	0.50	2.0

[a] Reaction $MgCl_2{\cdot}H_2O + H_2O = MgCl_2{\cdot}2H_2O$.
[b] Reaction $MgCl_2 + H_2O = MgCl_2{\cdot}H_2O$.
[c] Reaction $MgO + H_2O = Mg(OH)_2$.

Here we estimate this reduction for two extreme cases:

(a) adsorbate is completely exchanged near the rich isoster;
(b) adsorbate is completely exchanged near the weak isoster.

(a) According to the Clausius–Clapeyron equation for the gas pressure above adsorbent one can write

$$R\ \ln\left(\frac{P_c}{P_e}\right) = \Delta H_s\left(\frac{1}{T_c}-\frac{1}{T_2}\right),$$

where ΔH_s is the average sorption enthalpy.

Temperature T_2 can be estimated by the Trouton's rule that declares the intersection of adsorption isosters and liquid–gas equilibrium curve presented as $\ln P$ versus $1/T$ at $1/T \Rightarrow 0$ [4,5,7,10]:

$$T_2 = \frac{{T_c}^2}{T_e}.$$

This temperature relationship leads to a significant simplification of thermodynamic analysis. Now we can use the same computations as in the case of monovariant equilibrium for the COP of the cooling cycle:

$$\begin{cases} R\ \ln\left(\dfrac{P_c}{P_e}\right) = \Delta H_e\left(\dfrac{1}{T_e}-\dfrac{1}{T_c}\right) \\ R\ \ln\left(\dfrac{P_c}{P_e}\right) = \Delta H_s\left(\dfrac{1}{T_c}-\dfrac{T_e}{T_c^2}\right) \end{cases}$$

$$\Delta H_e\left(\frac{1}{T_e}-\frac{1}{T_c}\right) = \Delta H_s\left(\frac{1}{T_c}-\frac{T_e}{T_c^2}\right)$$

$$\begin{aligned} \mathrm{COP}^c &= \frac{\Delta H_e}{\Delta H_s} = \frac{(1/T_c)-(T_e/T_c^2)}{(1/T_e)-(1/T_c)} \\ &= \frac{T_e}{T_c}\left(\frac{(1/T_e)-(1/T_c)}{(1/T_e)-(1/T_c)}\right) = \frac{T_e}{T_c} \end{aligned} \qquad (11)$$

The difference

$$\mathrm{COP}_c^c - \mathrm{COP}^c = \frac{T_e}{T_g}\left(\frac{T_g-T_2}{T_c-T_e}\right) > 0,$$

hence the COP^c is lower than the Carnot COP_c^c.

Accordingly, for heating cycle $\mathrm{COP}^h = 1 + (T_e/T_c)$.

(b) The Clausius–Clapeyron equation for the weak isoster can be written as

$$R\ \ln\left(\frac{P_c}{P_e}\right) = \Delta H_s\left(\frac{1}{T_4}-\frac{1}{T_g}\right).$$

From the Trouton's rule $T_4 = T_g T_e/T_c$, so that

$$\begin{cases} R\ \ln\left(\dfrac{P_c}{P_e}\right) = \Delta H_e\left(\dfrac{1}{T_e}-\dfrac{1}{T_c}\right) \\ R\ \ln\left(\dfrac{P_c}{P_e}\right) = \Delta H_s\left(\dfrac{T_c}{T_e T_g}-\dfrac{1}{T_c}\right) \end{cases}$$

$$\Delta H_e\left(\frac{1}{T_e}-\frac{1}{T_c}\right) = \Delta H_s\left(\frac{T_c}{T_e T_g}-\frac{1}{T_c}\right)$$

$$\begin{aligned} \mathrm{COP}^c &= \frac{\Delta H_e}{\Delta H_s} = \frac{(T_c/T_e T_g)-(1/T_c)}{(1/T_e)-(1/T_c)} \\ &= \frac{T_c}{T_g}\left(\frac{(1/T_e)-(1/T_c)}{(1/T_e)-(1/T_c)}\right) = \frac{T_c}{T_g} < \mathrm{COP}_c^c \end{aligned} \qquad (12)$$

For heating cycle $\mathrm{COP}^h = 1 + (T_c/T_g)$.

For real 3T adsorption cycle the sorbate is exchanged in the temperature range between T_2 and T_g (desorption) and T_4 and T_c (adsorption). Brief analysis of this case is presented in Appendix A.

Thus, for divariant equilibrium, which takes place in an adsorption heat pump, there is inevitable degradation of the efficiency due to the thermal entropy production caused by the external thermal coupling of the isothermal heat reservoirs and sinks to the temperature varying adsorber. As a consequence, both the cooling and heating COP are always lower than the Carnot COP.

2. Conclusions

In this paper thermodynamic analysis of an ideal cycle of CHP and AHP was performed in order (a) to compare two definitions of the cycle efficiency used in literature, and (b) to estimate the maximal efficiency that can be reached for particular non-regenerative cycle. It was shown that the efficiency equal to the Carnot efficiency can be, in principle, obtained for a CHP, that results from a monovariant equilibrium of a gas–solid reaction. For a divariant equilibrium in an adsorption heat pump, the efficiency is always lower than the Carnot one due to the thermal entropy production caused by the external thermal coupling. This was demonstrated for various chemical gas–solid reactions and adsorbent–adsorbate working pairs with ammonia, methanol and water as working fluid. Simple estimation of the efficiency reduction was suggested.

Acknowledgements

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Table 2
The values of COP calculated as the ratio $\Delta H_c/\Delta H_s$ and according to Eq. (14) for various cooling cycles of AHP (error = $\{[\text{COP}_c - (H_c/H_s)]/(H_c/H_s)\} \times 100\%$)

Working pair	T_e (°C)	T_c (°C)	T_g (°C)	ΔH_s[a] (kJ/mol)	$\Delta H_c/\Delta H_s$	COP_c, Eq. (14)	Error (%)	COP_c^c
CH_3OH–carbon AC-35	0.0	17.0	44.7	45.85	0.88	0.93	+5.7	1.40
	0.0	17.0	53.0	46.66	0.86	0.92	+7.0	1.77
	0.0	17.0	62.5	46.17	0.87	0.90	+3.4	2.18
	0.0	17.0	72.0	47.49	0.85	0.89	+4.7	2.56
	0.0	17.0	78.2	47.52	0.85	0.88	+3.5	2.80
	0.0	17.0	82.7	48.14	0.84	0.88	+4.8	2.97
	0.0	17.0	90.1	48.10	0.84	0.87	+3.6	3.23
	0.0	17.0	101	47.01	0.86	0.86	0	3.62
CH_3OH–carbon ACLH	0.0	27.0	58.0	45.55	0.88	0.91	+3.4	0.95
	0.0	27.0	64.7	45.05	0.89	0.90	+1.1	1.13
	0.0	27.0	71.7	46.01	0.88	0.89	+1.2	1.31
	0.0	27.0	80.5	46.31	0.87	0.88	+1.2	1.53
	0.0	27.0	86.0	46.09	0.87	0.87	0	1.66
	0.0	27.0	91.7	46.70	0.86	0.87	+1.3	1.79
	0.0	27.0	100	47.30	0.85	0.86	+1.2	1.99
	0.0	27.0	115	46.90	0.86	0.84	−2.5	2.29
NH_3–carbon PX21 (MaxSorb)	5.0	35.7	124	30.01	0.84	0.77	−8.3	2.0
NH_3–H_2O	5.0	34.4	125	27.84	0.84	0.83	−1.2	2.01
H_2O–zeolite 13X	10.0	42.2	139	48.07	0.89	0.83	−6.7	2.06
H_2O–zeolite 4A	10.0	33.4	129	55.60	0.77	0.84	+9.1	2.87

[a] Average value.

Appendix A

For real 3T adsorption cycle the sorbate is exchanged in the temperature range between T_2 and T_g (desorption) and T_4 and T_c (adsorption). For preliminary estimation we can consider for COP the value that is average between those given by Eqs. (11) and (12), namely, for cooling

$$\text{COP}^c = \frac{1}{2}\left(\frac{T_e}{T_c} + \frac{T_c}{T_g}\right) \tag{13}$$

and for heating

$$\text{COP}^h = 1 + \frac{1}{2}\left(\frac{T_e}{T_c} + \frac{T_c}{T_g}\right).$$

For cooling COP^c

$$\begin{aligned}\text{COP}^c &= \frac{1}{2}\left(\frac{T_e}{T_c} + \frac{T_c}{T_g}\right) = \frac{1}{2}\left(\frac{T_e}{T_c} + \frac{T_c}{T_g}\right)\frac{(1/T_e)-(1/T_c)}{(1/T_e)-(1/T_c)} = \frac{1}{2}\left(\frac{(1/T_c)+(T_c/T_gT_e)-(T_e/T_c^2)-(1/T_g)}{(1/T_e)-(1/T_c)}\right)\\ &= \frac{1}{2}\left(\frac{(1/T_c)+(1/T_c)-(1/T_c)+(T_c/T_gT_e)-(T_e/T_c^2)-(1/T_g)-(1/T_g)+(1/T_g)}{(1/T_e)-(1/T_c)}\right)\\ &= \frac{1}{2}\left(\frac{[(2/T_c)-(2/T_g)]-[(1/T_c)-(T_c/T_gT_e)+(T_e/T_c^2)-(1/T_g)]}{(1/T_e)-(1/T_c)}\right)\\ &= \frac{(1/T_c)-(1/T_g)}{(1/T_e)-(1/T_c)} - \frac{1}{2}\left(\frac{(1/T_c)-(T_c/T_gT_e)+(T_e/T_c^2)-(1/T_g)}{(1/T_e)-(1/T_c)}\right)\\ &= \text{COP}_c^c - \frac{1}{2}\left(\frac{[(1/T_c)-(T_c/T_gT_e)]+[(T_e/T_c^2)-(1/T_g)]}{(1/T_e)-(1/T_c)}\right) = \text{COP}_c^c - \frac{1}{2}\left(\frac{a+b}{c}\right),\end{aligned} \tag{14}$$

where $a = (1/T_c) - (T_c/T_gT_e) = (1/T_c) - (1/T_4)$ is the length of isobar 4–1, and $b = (T_e/T_c^2) - (1/T_g) = (1/T_2) - (1/T_g)$ is the length of isobar 2–3 in the Clausius–Clapeyron co-ordinates, $c = (1/T_e) - (1/T_c)$. As $(a + b)/c$ is positive, the COP^c is always less than the Carnot COP_c^c, and the difference increases with the temperature range between the rich and weak isosters.

Eq. (14) can be applied for simple estimation of the COP^c for real 3T cycles of AHPs. We analyzed the accuracy of this estimation for various working pairs [11,12] with methanol, ammonia and water as adsorbates (Table 2). Regardless the nature of adsorbent and adsorbate, the COP calculated by Eq. (14) appeared to be close to the ratio of $\Delta H_c/\Delta H_s$, the relative difference is being less than 9%.

It is worthy to note that this approach could be extended for analysis of sorption cycles based on liquid absorption, as it is done for working pair NH_3–water displayed in Table 2 as well.

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