

Thermodynamics Analysis of Adsorption Refrigerator

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Abstract: Sorption cooling systems are the most promising technology in the area of heat driven heat pump or refrigerator technology. In this article, the entropic analysis is developed for these virtual systems showing that they are irreversible. A thermodynamic analysis is first developed that emphasizes adsorption refrigerator thermodynamics analysis for fixed adsorption bed, and demonstrate how the heat and mass equation of state can be calculated from thermodynamic properties of the bulk phase being in equilibrium with the adsorbate. Then we formulate balance equations and considering the second law of thermodynamics for gaseous bulk phase adsorbate phase and a solid phase. In addition, establish constitutive equations for heat and mass exchange of the system with the surrounding bulk phase, fixed adsorption bed work lose for isothermal adsorption or desorption processes.

Keywords: adsorption, fixed adsorption bed, entropy, mass transfer, energy transfer

NOMENCLATURE

Symbol	Description [Units]
T	Temperature [K]
P	Pressure [Pa]
ρ	Density [kg/m^3]
c	Specific heat capacity [$\text{J}/(\text{kg} \cdot \text{K})$]
R	Specific gas constant [$\text{J}/(\text{mol} \cdot \text{K})$]
S	Entropy [J/kg]
U	Internal energy [J/kg]
U/h	Enthalpy [J/kg]
G	Gibbs-free energy [J/kg]
σ	Surface tension [$\text{N}/\text{m} \times 10^2$]
μ	Chemical potential [J/kg]
τ	Time [s]
A	Area [m^2]
A_s	Specific surface [m^2/kg]
A_q	Surface [m^2/kg]

1. INTRODUCTION

At present, adsorption refrigerator technology has been aroused attention in our refrigeration industry. It is commonly accepted that the refrigeration industry is facing a new challenge: it must continue developing refrigeration applications, especially in the developing countries without increasing anymore the ecological dangers: depletion of the ozone layer and global warming. In order to protect the ozone layer, CFC-free conventional compression systems have currently been banned in the next decades in the world. In the promotion of environmentally friendly energy utilization systems, adsorption refrigerator has a promising potential for environmental protection and energy economy. In the field of environment-friendly cooling process, solid-vapour adsorption and liquid-vapour adsorption are likely alternatives to traditional

compression, at least for the applications where cold is produced at temperature lying over 0°C [1]. So adsorption refrigerator technologies get enough recognition.

It is well known that physical adsorption in fixed bed is always coupled with some heat generation. In all cooling cycle, the performances are far from the ideal Carnot cycle performance. A first-law analysis does not tell us why there is this performance degradation, it only analyzes the loss on the quantity for adsorption refrigerator [2]. Therefore, a second-law analysis is necessary for adsorption refrigeration to tell the reasons for that degradation. Moreover, the first law states that in every cyclic process either work is converted into heat or heat is converted into work. The second law, on the other hand, marks the distinction between these two quantities by stating that heat from a single source whose temperature is uniform cannot be completely converted into work in any cyclic process, whereas work from a single source can always be completely converted into heat.

To intensify heat and mass transfer in adsorbents for getting higher performances for adsorption bed, one way is to produce a solid adsorbent shape and to build consolidated adsorbent. In this article, we take a fixed adsorption bed for example.

2. THERMOSTATIC OF ADSORPTION BALANCE EQUATIONS

2.1 Thermostatics of adsorption

Adsorption processes research are becoming more and more important in various fields of science and engineering. Adsorption processes always are combined with thermal effects, which is heating or cooling of the adsorbent. Adsorption is a kind of interface phenomenon. Since the molecule usually loses some of its degrees of freedom on adsorption as compared

with the gaseous state, and the adsorbed state is characterized by a higher degree of order, which is signified by the condition $\Delta S < 0$ (entropy change) for an inert adsorbent. The adsorbent surface adsorbs the gas is a process which interface area constant decrease in the adsorption process, self-moving process that the interface tension reduce.

We consider a fixed adsorption bed including a fluid, which is liquid or gaseous bulk phase (adsorptive (f)), an adsorbed phase (adsorbate(a)) and a solid phase(adsorbent(s)). This model is shown in Figure 1.

The adsorption process now can be assigned various thermodynamic quantities like the internal energy U , enthalpy H , Gibbs' free enthalpy G , entropy S and so on. Moreover, we can assign intensive thermodynamic parameters, for example, temperature T , pressure P , chemical potential μ and surface tension σ being connected by Gibb's equation as follow

$$dS = \frac{1}{T} dU + \frac{P}{T} dV + \frac{\sigma}{T} dA - \sum \frac{\mu_i}{T} dn_i$$

Here A is the surface acreage of the interface. We here assumed the volumes of the fluid and solid phase to be constant. Moreover, the solid adsorbent to be rigid and inert, which is to have constant surface.

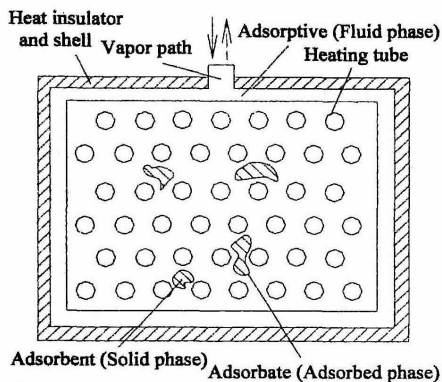


Figure 1: The fluid phase (f), adsorbed phase (a) and solid phase (s) inside absorber.

The thermodynamic approach to the study of equilibrium is quite general and may be applied to adsorption just as to any other phase equilibrium. The only general assumption which is implicit in such an approach is that the adsorbed layer can be treated as a distinguishable phase in the thermodynamic sense. Therefore, thermodynamic equilibrium and non-equilibrium states of any of the phases (f, a, s) can phenomenon logically be described by the usual extensive and intensive variables which are connected by the Gibb's equation as follows

$$dS^f = \frac{1}{T^f} dU^f - \frac{\mu^f}{T^f} dn^f \quad (1)$$

$$dS^a = \frac{1}{T^a} dU^a + \frac{\sigma^a}{T^a} dA - \frac{\mu^a}{T^a} dn^a \quad (2)$$

$$dS^s = \frac{1}{T^s} dU^s \quad (3)$$

Here A is the surface of the adsorbed phase. The superscript f denotes the adsorptive phase, the superscript a denotes adsorbed phase and the superscript s denotes adsorbent phase.

2.2 Balance equation

Let us consider the combined system of a fixed adsorption bed adsorption column. The mass of the adsorbent is constant, $n^s = \text{const}$, we here ignored kinetic energy and potential energy of adsorptive. The balance equations for mass and energy of this system read

$$\frac{d(n^f + n^a)}{d\tau} = \frac{dn}{d\tau} = J \quad (4)$$

$$\frac{d(U^f + U^a + U^s)}{d\tau} = \frac{dU}{d\tau} = \frac{\delta Q}{d\tau} + h^f J \quad (5)$$

Here τ is time variable, J indicates influx adsorption bed special mass flux. Q indicates exterior exchange of fixed adsorption bed with cooling fluid.

3. CONSTITUTIVE EQUATIONS FOR MASS AND ENERGY TRANSFER

3.1 The second law of thermodynamics

Consider an adsorption process of adsorption which starts at time $\tau = -\infty$ in one equilibrium state and ends at $\tau = \tau$ in another equilibrium state for fixed adsorption bed. Suppose each phase near to a certain and equilibrium state in any time. For such a process the second law of thermodynamics states

$$\int_{-\infty}^{\tau} \left[\frac{dS^f}{d\tau} + \frac{dS^a}{d\tau} + \frac{dS^s}{d\tau} - \frac{\delta Q}{T_i} - s^f J \right] d\tau \geq 0$$

Here S^f denotes the specific entropy of the adsorptive. T_i denotes exterior fluid temperature of adsorption bed. Inserting Gibbs' equation (1-3) and the conservation laws (4-5) and taking $A = \text{const}$ and $T^a = T^s = T$ into account, we get

$$\int_{-\infty}^{\tau} \left[\left(\frac{1}{T^f} - \frac{1}{T_i} \right) \frac{dQ}{d\tau} + \left(\frac{1}{T} - \frac{1}{T^f} \right) \left(\frac{dU^a}{d\tau} + \frac{dU^s}{d\tau} \right) \right] d\tau + \int_{-\infty}^{\tau} \left[\left(\frac{\mu^f}{T^f} - \frac{\mu^a}{T} \right) \frac{dn^a}{d\tau} \right] d\tau \geq 0 \quad (6)$$

Obviously, the first term describes exterior heat transfer of adsorption bed, the second term describes the internal energy transfer between gaseous bulk phase and adsorbed phase, the last one describes mass transfer between gaseous bulk phase and adsorptive phase.

Reference as literature [3], above inequality can be regarded as describes the thermodynamic forces and flux relations of irreversible processes. For real processes the thermodynamic fluxes can't be independent from the respective forces which we abbreviate by

$$\begin{aligned} X &= \frac{1}{T^f} - \frac{1}{T_i} \\ X_u &= \frac{1}{T} - \frac{1}{T^f} \\ X_m &= \frac{\mu^f}{T^f} - \frac{\mu^a}{T} \end{aligned}$$

Here X indicates exterior heat transfer force of adsorption bed, X_u indicate interior energy exchange force between gaseous bulk phase and adsorbed phase, X_m indicates mass transfer force between gaseous bulk phase and adsorptive phase. In ordinary thermodynamics of irreversible processes the constitutive equations reduce in the simplest case to linear relations as follow:

$$\frac{\delta Q}{d\tau} = k_\alpha A_q \left(\frac{1}{T^f} - \frac{1}{T_i} \right) \quad (7)$$

$$\frac{dU^a}{d\tau} + \frac{dU^s}{d\tau} = k_\alpha A_q \left(\frac{1}{T} - \frac{1}{T^f} \right) \quad (8)$$

$$\frac{dn^a}{d\tau} = k_\beta A_s \left(\frac{\mu^f}{T^f} - \frac{\mu^a}{T} \right) \quad (9)$$

Here K_α indicate heat transfer coefficient, K_β indicate Mass transfer coefficient. Cross-effects between heat and mass transfer have been neglected in (8-9) since the respective transport coefficients. Generally this will not be true. However, a decision of this question requires accurate experiments on adsorption processes. In this here we only account for this irreversible processes, Cross-effects between heat and mass transfer is very difficult measure and validate by experiment [3].

3.2 Constitutive equation of fixed adsorption bed

The chemical potential of the ideal adsorptive and adsorbate at temperature T^f and pressure P^f can be written as

$$\frac{\mu^f(T^f, P)}{T^f} = \frac{\mu^f(\hat{T}, \hat{P})}{\hat{T}} - c_p^f \ln\left(\frac{T^f}{\hat{T}}\right) + R \ln\left(\frac{P^f}{\hat{P}}\right) \quad (10)$$

$$\frac{\mu^a(T, P)}{T} = \frac{\mu^f(\hat{T}, \hat{P})}{\hat{T}} - c_p^f \ln\left(\frac{T}{\hat{T}}\right) + R \ln\left(\frac{P}{\hat{P}}\right) \quad (11)$$

Where $\hat{P}$ and $\hat{T}$ indicate the pressure and temperature of a reference state [4]

The internal energy U of the adsorptive is assumed to be adequately described by the simple equation [4]

$$U^f = \hat{U}^f + cn^f(T^f - \hat{T}) \quad (12)$$

The constitutive equations (7-9) together with the balance equations (4,5) in view of (10,11) lead to the differential equations

$$J = k_\beta A_s \left(-c_p^f \ln\left(\frac{T^f}{T}\right) + R \ln\left(\frac{P^f}{P}\right) \right) + \frac{dn^f}{d\tau} \quad (13)$$

$$\frac{dU}{d\tau} = k_\alpha A_q \left(\frac{1}{T} - \frac{1}{T_i} \right) + h^f J \quad (14)$$

describing the growth rate of the mass and internal energy of a fixed adsorption bed due to heat exchange with exterior exchange fluid. If we think $n^f = \text{const}$ that is n^f isn't change with time, so equation (13) becoming

$$J = k_\beta A_s \left(-c_p^f \ln\left(\frac{T^f}{T}\right) + R \ln\left(\frac{P^f}{P}\right) \right) \quad (15)$$

Considered phase equilibrium between the adsorptive and the adsorbate, which is $\mu^a = \mu^f = \mu$ and $T^f = T$, so inequality (6) becomes

$$\int_{-\infty}^{\tau} \left(\frac{1}{T} - \frac{1}{T_i} \right) \frac{\delta Q}{d\tau} d\tau \geq 0 \quad (16)$$

If we consider isothermal adsorption processes, because the entropy production is equal the entropy flow for isolating system, integrate inequality (16) we have

$$S_{gen} = \left(\frac{1}{T} - \frac{1}{T_i} \right) Q$$

Here S_{gen} indicates system entropy produce. We think environment temperature is T_0 . when system came though irreversible processes, working loss of fixed adsorption bed is

$$E_{deg} = T_0 \left(\frac{1}{T} - \frac{1}{T_i} \right) Q \quad (17)$$

Here E_{deg} indicates system work loss of fixed adsorption bed. This is adsorption bed work loss for isothermal adsorption or adsorption processes.

3.3 Equations explicitly of adsorption process

In the thermodynamic analysis of adsorptive phase for fixed adsorption bed, P and T are the most convenient intensive variables, and since the criterion for equilibrium at constant P and T is minimum Gibbs-free energy, equilibrium relationships are generally developed in terms of G .

Generally speaking, we should know state parameters of gaseous bulk phase for adsorption process, for example, P , T , c , H and n' . For an adsorbed phase, pressure P is not a significant intensive variables. Then we can calculate the other parameters of an adsorbed phase. These parameters can be calculated as follow. Assume the state of the gaseous bulk phase for fixed adsorption bed, for example, all thermodynamic parameters of all phase (f, a, s) to be given at any (initial) time τ . Then, from the thermostatic equations of state of the single phase include in equations (1-3) and properly of chosen differential equation (7-9) inserted in the differential equations(4,5), the extensive quantities n, U of phases f, a, s , at time $(\tau + \Delta \tau)$ and from them the respective intensive parameters for temperature T at the same time can be calculated. This determines the thermodynamic state of the fixed adsorption at $(\tau + \Delta \tau)$. Certainly, we should take of advantage iterative procedure calculated those variables when work on this process. We can also take advantage of equation (17) calculate the total work lose of adsorption bed for adsorption processes^[3,4,5].

Here we do not give more detail. Author thinks much work or more important things are analysis thermodynamic processes for adsorption bed by Gibbs equation. Moreover, we give a way to instruct experiment that is forecast experiment results by numerical calculate results. It is also very good mean to improve on experiment mode and measure.

4. CONCLUSION

In this article, author deduced heat and mass transfer differential equation for fixed adsorption bed from the theories by the second law of thermodynamics and the Gibb's equation, and establish constitutive equations for heat and mass exchange of the system with the exterior fluid. Get

adsorption or desorption processes entropy produce and work lose for fixed adsorption bed. Furthermore, those equations establish could provide some experiment results forecast in order to improve on experiment measures.

REFERENCES

- [1] Tovbin, Yu. K 1999. Analysis of thermal desorption spectra of heterogeneous surfaces. May 6-11. West Germany. Langmuir. v 15, n 18, Aug.
- [2] Pons, M.2000. Entropic analysis of adsorption open cycles for air conditioning. Part 1: first and second law analyses. International Journal of Energy Research, v 24, n 3, Mar, p 251-262.
- [3] Keller, J. U.1984. Consequences form the second law of thermodynamics for the dynamics of adsorption processes. Engineering Foundation, p 259-265.
- [4] Keller, J.U. 1988. Thermodynamics of nonsothermal adsorption processes. Journal of Non-Equilibrium Thermodynamics, v13, n2, p 161-176.
- [5] Pons, M.1997 Analysis of the adsorption cycles with thermal regeneration based on the entropic mean temperatures. Applied Thermal Engineering, v 17, n 7, Jul, 1997, p 615-627.
- [6] Everett, Douglas H.1984. Thermodynamics of adsorption form solution. Engineering Foundation, p1-22.
- [7] Kokotov, Y. A.1995. Methods of thermodynamic description of the surface layer in relation to the problem of measured quantities in the thermodynamics of adsorption. Russian Journal of Physical Chemistry, v 69, n12, p20-42.
- [8] Pons, M.1996. Second law analysis of adsorption cycles with thermal regeneration. Journal of Energy Resources Technology, Transactions of the ASME 118 3 Sep, ASME, p 229-236.
- [9] Ai-min, Li. 2004 Thermodynamic study of adsorption of phenolic compounds from aqueous solution by a water-compatible hypercrosslinked polymeric adsorbent. Chinese Journal of Polymer Science, v 22, No 3, P 259-267.