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# THE SPECIFIC HEAT CAPACITY OF ADSORBATE-ADSORBENT SYSTEM

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## ABSTRACT

The complete thermodynamic property fields for a single-component adsorbent + adsorbate system, which enables us to compute for the specific heat capacity, partial enthalpy and entropy has been developed. The specific heat capacity of the adsorbent-adsorbate system is comprised of two parts; one is the specific heat of solid adsorbent and the other is the contribution of adsorbate at different isothermal conditions. Conventionally, the specific heat capacity of the adsorbate is simply assumed to correspond to its liquid phase specific heat capacity and more recently to that of its gas phase. In this paper, we propose a simple but improved expression for the adsorbate specific heat capacity that is underpinned by first-principle analyses. This expression will be shown to be adequate for the design of adsorbent beds.

## 1. INTRODUCTION

The adsorption characteristics of adsorbates on adsorbents are essential in the field of separation process, purification of gases, adsorption chillers, cryocoolers design and more recently hydrogen storage. The physical adsorption process occurs mainly within the pores of adsorbent and the external adsorbent surface. The knowledge of thermodynamic property fields of adsorbent plus adsorbate system is important, because it enables the adsorption process to be analyzed. In this paper, the complete formulations of some thermodynamic properties such as internal energy, partial enthalpy, and partial entropy have been developed to understand the specific heat capacity of a single component adsorbate + adsorbent system. The present formulation of specific heat capacity as a function of pressure, temperature, and mass of adsorbate, has been developed for a single component adsorbent + adsorbate (or adsorbate + adsorbent) system, and thermodynamic equilibrium prevails between this system and single-component unadsorbed gas phase. We shall make use of experimental isotherm data available from the literature that are of practical interest to highlight the significant difference between the conventional uncorrected form of the specific heat capacity and the improved simplified expression presented herein.

## 2. THE FORMULATION OF SPECIFIC HEAT CAPACITY OF ADSORBATE-ADSORBENT SYSTEM

The full expressions of the total differential extensive thermodynamic quantities (enthalpy, internal energy and entropy) of a single component adsorbate + adsorbent system (Chua et al., 2003) at a constant mass of adsorbent,  $M_{abe}$ , are expressed as follows

$$dH(P, T, m_a, M_{abe}) = M_{abe} c_{p,abe} \cdot dT + m_a \left[ c_{p,g}(P_1, T) + \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] dT + [h_g(P_1, T) - \Delta H_{ads}] dm_a + \frac{M_{abe}}{\rho_{abe}} dP \quad (1)$$

$$dU(P, T, m_a, M_{abe}) = M_{abe} c_{p,abe} dT + m_a \left[ c_{p,g}(P_1, T) + \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] dT + [h_g(P_1, T) - \Delta H_{ads}] dm_a \quad (2)$$

and

$$dS(P, T, m_a, M_{abe}) = M_{abe} c_{p,abe} \frac{dT}{T} + m_a \left[ c_{p,g}(P_1, T) + \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] \frac{dT}{T} + \left[ s_g(P_1, T) - \frac{\Delta H_{ads}}{T} \right] dm_a \quad (3)$$

The first term on the right-hand side of Equations (1), (2) and (3) refers to the thermodynamic property of adsorbent and the second and third terms to that of the adsorbate in the system. Equation (1) is important for the analysis of the energy transfer associated with a typical adsorption / desorption process where the volume of the adsorbent-adsorbate system does not change significantly during the process. It is therefore interesting to note that the difference between the conventionally used expression for the differential internal energy and equation (1)

is  $m_a \left[ \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] dT + [h_g \{P_1(T, m_a)\} - h_g(P, T)] dm_a$ . Similarly, the difference between the conventionally used expression for the differential entropy and equation (3) is  $m_a \left[ \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] \frac{dT}{T} + [s_g \{P_1(T, m_a)\} - s_g(P, T)] dm_a$ .

The specific heat capacity of the adsorbate has for a long time been assumed to be equal to the liquid phase specific heat capacity (Ruthven, 1984 and Suzuki, 1990). Recently some researchers (Myers, A.L, 2002, Saha et al., 1995, Sami et al., 1996, Chua et al., 1998) view the specific heat capacity of the adsorbate to be equal to the gas phase specific heat capacity. These are defined as,

$$c_{ls} = c_{p,abe} + \frac{m_a}{M_{abe}} c_{p,l}(P_1, T) \quad (4)$$

$$c_{gs} = c_{p,abe} + \frac{m_a}{M_{abe}} c_{p,g}(P_1, T) \quad (5)$$

We propose that the specific heat capacity of the adsorbent + adsorbate system can be adequately represented by,

$$c_{as} = c_{p,abe} + \frac{m_a}{M_{abe}} \left[ c_{p,g}(P_1, T) + \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right] \quad (6)$$

The correction due to  $m_a \left[ \frac{\Delta H_{ads}}{T} - \frac{\Delta H_{ads}}{v_g} \frac{\partial v_g}{\partial T} \right]$  turns out to be significant, because of the large isosteric heat of adsorption and the non-ideality of the gas phase. This term represents the effect of the adsorbent in the adsorbed phase. The newly interpreted specific heat capacity can be significantly different from the gas phase specific heat capacity and equation (5) reduces to equation (4) in the limit of low pressure and high temperature.

The difference between the newly interpreted specific heat capacity and the specific heat capacity which assumes a gaseous phase adsorbate of a single-component adsorbent + adsorbate system is written as

$$\Delta c_p = |c_{as} - c_{gs}| \quad (7)$$

### 3. RESULTS AND DISCUSSION

Some researchers assume that the adsorbate is in a liquid state (Ruthven, 1984 and Suzuki, 1990) and more recently some regard the adsorbate as a vapor phase (Myers, A.L, 2002, Saha et al., 1995, Sami et al., 1996, Chua et al., 1998) in their design of adsorption processes. We calculated three different specific heat capacities, namely the newly interpreted specific heat capacity, the specific heat capacity assuming gaseous adsorbate, and specific heat capacity assuming liquid adsorbate phase in a single-component adsorbent + adsorbate system. Representative experimental isotherm data obtained from the literature are used in the demonstration of the correction to the system specific heat capacity offered by our proposed expression. These pertain to silica gel + water vapor (Chua et al.,

2002), activated carbon + nitrogen (Prasad et al., 1996), activated carbon + hydrogen (Benard et al., 2001), activated carbon + neon (Chan et al., 1984), and activated carbon + HFC134a (Akkimaradi et al., 2001) systems. For activated charcoal + HFC134a system, the specific heat capacity assuming liquid adsorbed phase is included in the comparison. But for activated carbon + nitrogen and activated carbon + hydrogen systems, the specific heat capacity assuming liquid phase is excluded, as the adsorbed states are above the critical ranges. Figure 1 shows the specific heat capacities of chemviron charcoal + HFC 134a system. Three different types of heat capacities are plotted here at a 293 K and 353 K respectively. One could observe that  $c_{ls}$  is very close to  $c_{as}$  at low pressure and  $c_{ls}$  is consistently higher than  $c_{as}$  and  $c_g$  at higher pressure, and the correction offered by  $c_{as}$  could be as high as 11% at 293 K. For activated charcoal + HFC134a systems, out of the three types of activated charcoal which Akkimaradi et al. reported, the maximum  $\Delta c_p$  for Maxsorb activated charcoal is about 38% and for Fluka activated charcoal is about 12%.

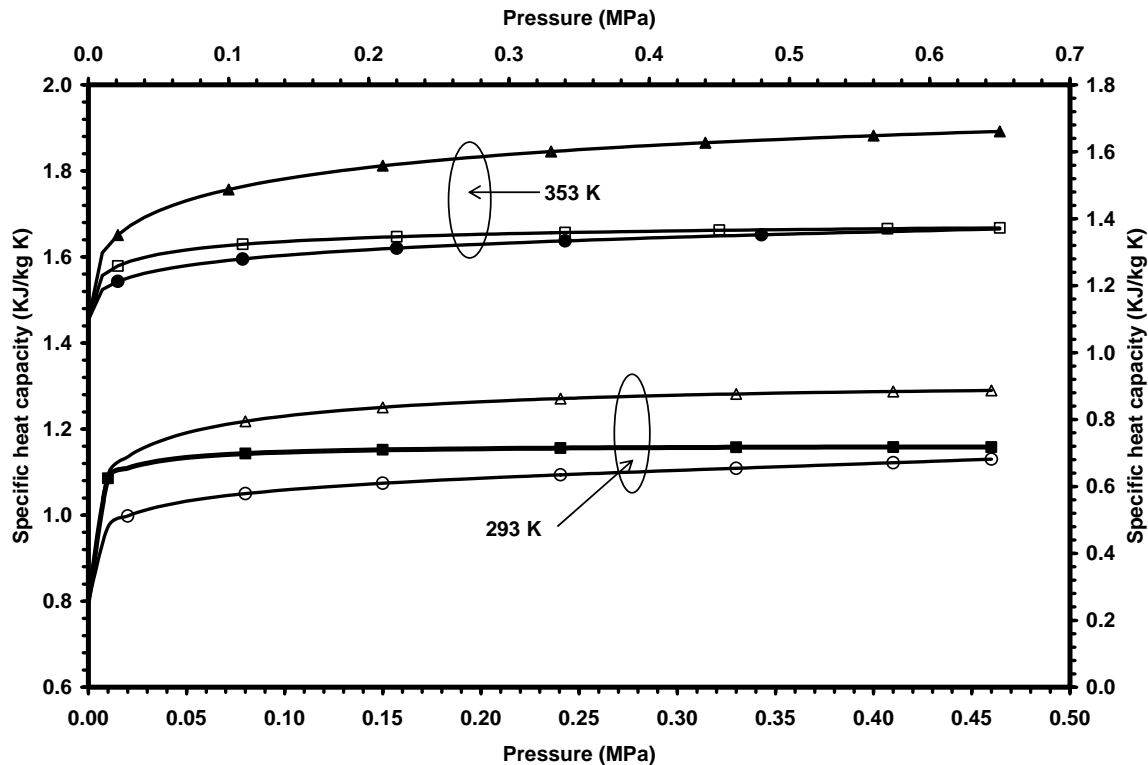


Figure 1: Specific heat capacities of chemviron charcoal + HFC134a system when adsorption temperature is 293 K: data points (■) denote the newly expressed specific heat capacity, (○) defines the specific heat capacity at gas phase adsorbate and (△) indicates the specific heat capacity at liquid phase adsorbate, when adsorption temperature is 353 K: the data points (□) denote the newly expressed specific heat capacity, (●) defines the specific heat capacity at gas phase adsorbate and data points (▲) refer to the specific heat capacity at liquid phase.

Figure 2 shows the plot of specific heat capacities of activated carbon + nitrogen system at temperatures 210 K and 360 K respectively, where  $\Delta c_p$  is very significant. At 210 K, the value  $\Delta c_p$  ranges from 5% to 14 % but at 360 K or the high temperature isotherm, the value  $\Delta c_p$  decreases to about 1 %. The specific heat capacities of activated carbon + hydrogen at temperatures 90 K and 170 K are plotted against pressures in Figure 3.  $\Delta c_p$  (up to 5%) is significant at low temperature isotherm 90 K, but at 170 K the value  $\Delta c_p$  becomes nearly zero.

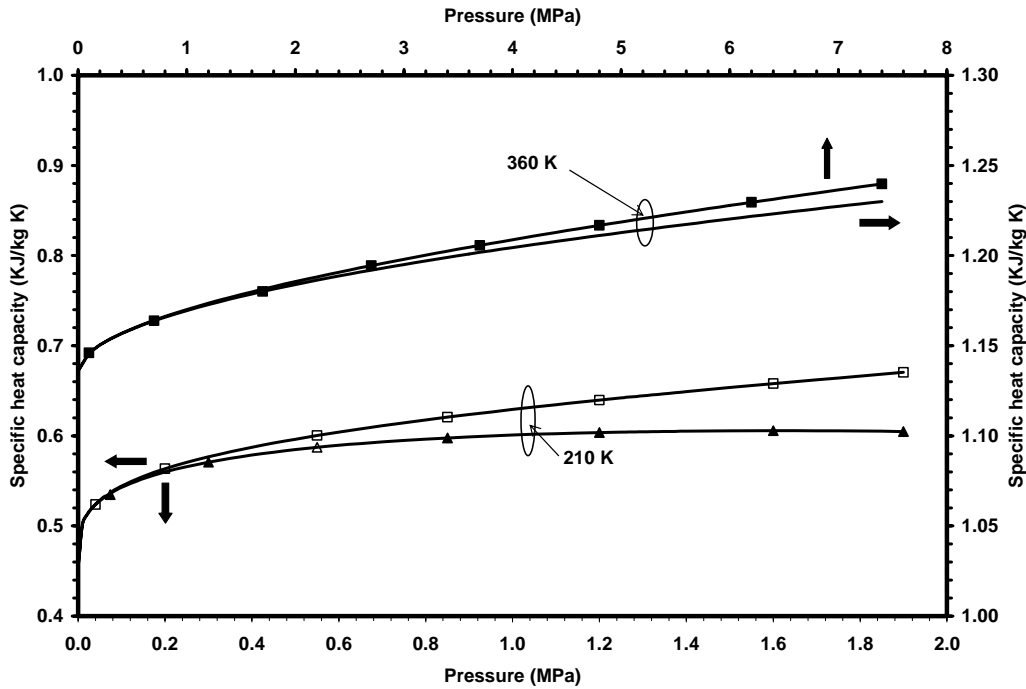


Figure 2: Specific heat capacities of activated charcoal + nitrogen system at different states when adsorption isotherm temperature is 210 K: data points ( $\blacktriangle$ ) refer to the newly derived specific heat and ( $\square$ ) defines the specific heat capacity when the adsorbate is in gaseous phase, when adsorption temperature is 360 K: data points ( $\text{---}$ ) denote the newly interpreted specific heat capacity and ( $\blacksquare$ ) defines the gas phase adsorbate specific heat capacity.

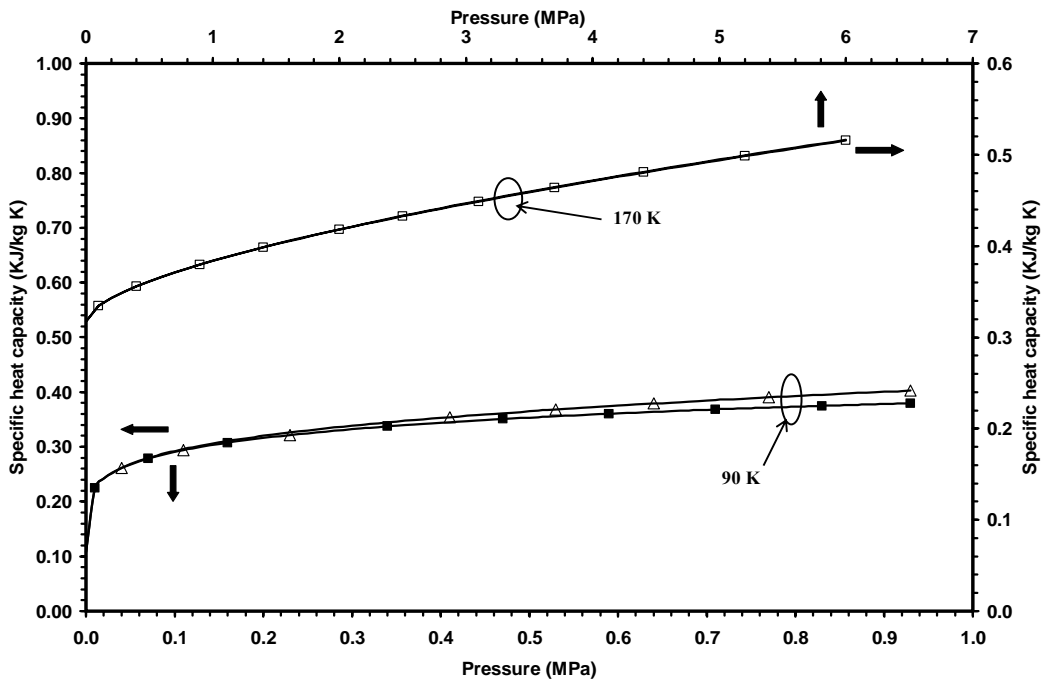


Figure 3: Specific heat capacities of activated charcoal + hydrogen system when adsorption temperature is 90 K: data points ( $\blacksquare$ ) denote the newly expressed specific heat capacity and ( $\triangle$ ) defines the specific heat capacity at gas phase adsorbate, when adsorption temperature is 170 K: data points ( $\square$ ) denote the newly expressed specific heat capacity and the thick line ( $\text{---}$ ) defines the specific heat capacity at gas phase adsorbate.

The newly proposed form of specific heat capacity and the conventionally used form of specific heat capacities of a single component activated carbon + neon are plotted in Figure 4. The value  $\Delta c_p$  varies from 5% to 14% with pressure (from 0.3 MPa to 1.6 MPa) at low temperature (90 K) but at 170 K,  $\Delta c_p$  is nearly equal to zero.

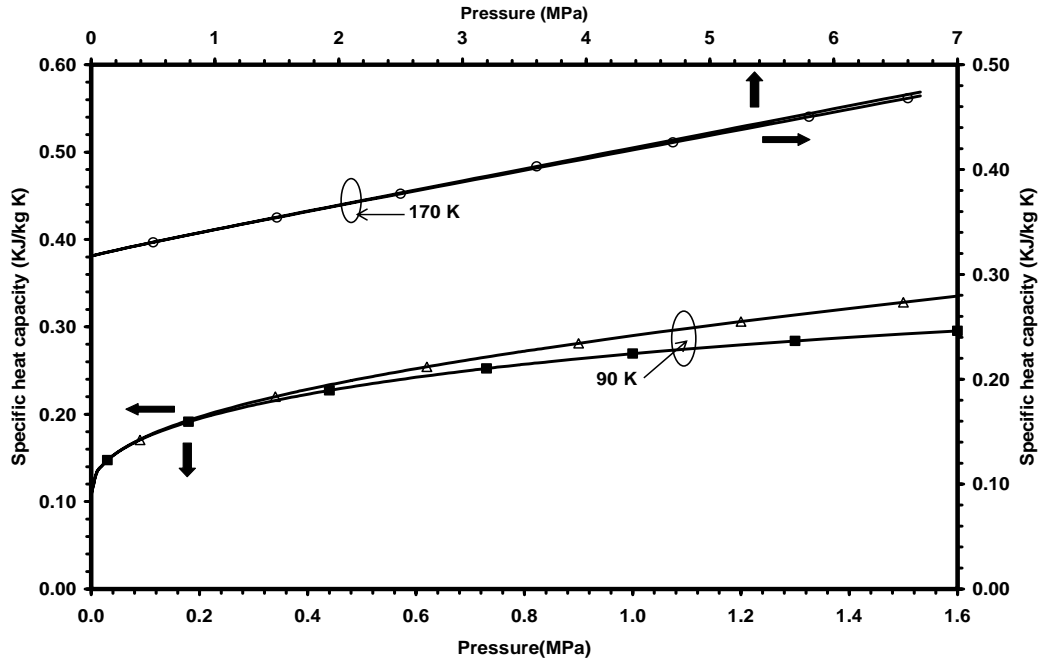


Figure 4: Specific heat capacities of activated charcoal + neon system when adsorption temperature is 90 K: data points (■) denote the newly expressed specific heat capacity and (Δ) defines the specific heat capacity at gas phase adsorbate, when adsorption temperature is 170 K: the thick line (—) denote the newly expressed specific heat capacity and the dotted line (○) defines the specific heat capacity at gas phase adsorbate.

#### 4. CONCLUSIONS

The formulation of specific heat capacity of a single component adsorbent + adsorbate system is one of the basic foundations of any adsorbate-adsorbent thermodynamic analysis. Such a key thermodynamic quantity is essential in the development of adsorption thermodynamics and this would be useful in the design and analysis of solid-gas sorption in cooling applications such as adsorption chiller, adsorption cryocoolers, infrared detectors cooling. We have demonstrated that the error made in earlier expressions of specific heat capacities can be significant at high pressures and lower temperatures especially for large adsorbate molecules that are of practical interests.

#### NOMENCLATURE

$P$	Pressure	MPa	<b>Subscripts</b>
$P_1$	Saturated pressure	MPa	$g$ gas phase
$T$	Temperature	K	$a$ adsorbate
$M, m$	mass	kg	$abe$ adsorbent
$\Delta H_{ads}$	Isosteric heat of adsorption	J/kg	$ls$ liquid state
$h$	specific enthalpy of adsorbate	J/kg	$gs$ gaseous
$H$	enthalpy	J/kg	$as$ actual state

$U$	internal energy	J/kg
$S$	entropy	J/kg K
$\rho$	density	kg/m <sup>3</sup>
$c_p$	specific heat capacity	KJ/kg K
$c$	specific heat capacity of adsorbate-adsorbent system	KJ/kg K
$v$	specific volume	m <sup>3</sup> /kg

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## REFERENCES

- Chua, Hui. T, Kim C. Ng, Anutosh Chakraborty and Nay M. Oo, 2003, Thermodynamic property fields of adsorbate-adsorbent system, *Langmuir*, Vol., 19, p. 2254-2259.
- Ruthven, D.M. 1984, *Principles of adsorption and adsorption processes*, John Wiley & Sons, New York, USA.
- Suzuki, M., 1990, *Adsorption engineering* Elsevier, Amsterdam, the Netherlands.
- Myers, A.L, 2002, Thermodynamics of Adsorption in Porous Materials, *AIChE Journal*, Vol. 48, No. 1, p.145-160.
- Saha, B.B, E.C. Boelman, and T. Kashiwagi, 1995, Computer simulation of a silica gel water adsorption refrigeration cycle-the influence of operating conditions on cooling output and COP, *ASHRAE Trans, Research*, Vol. 101, No.2, p.348-357.
- Sami, S.M. and C. Tribes, 1996, An improved model for predicting the dynamic behaviour of adsorption systems, *Applied Thermal Engineering*, Vol. 16, No. 2, pp. 149-161.
- Chua, H.T., K.C. Ng, A. Malek, T. Kashiwagi, A. Akisawa, and B.B. Saha, 1998, Modeling the performance of two-bed, silica gel-water adsorption chillers, *Int. J. Refrig.*, Vol. 22, pp. 194-204.
- Chua, Hui. T, Kim C. Ng, Anutosh Chakraborty, Nay M. Oo, and Mohamed A. Othman, 2002, Adsorption Characteristic of Silica gel + water Systems, *Journal of Chemical and Engineering data*, Vol. 47, p. 1177-1181.
- Prasad, M, B.S. Akkimardi, S.C. Rastogi, R.R. Rao, and K. Srinivasan, 1996, Adsorption Characteristic of the Charcoal-Nitrogen system at 79-320 K and pressures to 5 MPa, *Carbon*, Vol. 34, No.11, p.1401-1406.
- Benard, P, and R. Chahine, 2001, Determination of the Adsorption Isotherms of Hydrogen on Activated Carbons above the Critical Temperature of the Adsorbate over wide temperature and pressure ranges, *Langmuir*, Vol.17, p.1950-1955.
- Chan, C.K, E. Tward, and K.I. Boudaie, 1984, Adsorption isotherms and heats of adsorption of hydrogen, neon, and nitrogen on activated charcoal, *Cryogenics*, p.451-459.
- Akkimaradi, B.S., M. Prasad, P. Dutta, and K. Srinivasan. 2001, Adsorption of 1,1,1,2-tetrafluoroethane on activated charcoal, *Journal of Chemical and Engineering Data*, Vol. 46, No. 2, p. 417 -422.
- Prakash M. Jose, A. Mattern, Madhu Prasad, Sant Ram, Subramanya, and K. Srinivasan, 2000, Adsorption parameters of activated charcoal from adsorption studies, *Carbon*, Vol. 38, p. 1163-1168.