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Short communication

Interpretation of Gibbs surface excess model for gas adsorption on heterogeneous coal particle

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ABSTRACT

Sorption kinetics measurement is the essential prerequisite of constructing adsorption isotherms in the research field of coalbed methane production and CO_2 injection, however, Difficulty arises from the fact that sorption kinetics measurement is found to be accompanied by thermodynamic effect (e.g. fluctuation of temperature and pressure); that is, it has a strong dependence on the accuracy of models and methods of adsorption isotherm. In this regard, a new model analogous to Gibbs surface excess (GSE) adsorption is presented in this study for gas adsorption on heterogeneous coal particle in the interest of interpretation and application the GSE theory to the sorption kinetics measurement. According to this model, alternative method of adsorption isotherm calculation is developed in this paper, which suggests that thermodynamic parameters of adsorption measurement are detected in a contrasting and synchronous manner and thus enable the validity of adsorption data to be judged more accurately. Furthermore, feasibility tests were performed and results showed that the current model and method of adsorption isotherm determination could be used to improve experimental accuracy for the integral and incremental sorption step measurements.

1. Introduction

The increasing concern on the enhanced coalbed methane (ECBM) production and CO_2 injection has resulted in growing interest in carrying out gas sorption kinetic experiments and interpreting the adsorption and diffusion behavior of coal. The mainstream method for such experiments called volumetric method, had been applied to a significant amount of work [1–15], has an similarly experimental installation consisting of expanding a given gas from a reference cell of known volume into an evacuated sample cell containing known mass of sieved coal particles (see Fig. 1). Review of most previous studies shows that the volumetric method measurements can be divided into two forms: the single/integral sorption step measurement (abbreviated as SSS) [3–6,8–10] and the incremental sorption steps measurement (abbreviated as ISS) [11–15]. The SSS measurement fully injected gas into an evacuated coal sample to a selected pressure at a chosen set point and performed by many researchers to execute only an isotherm in one test, while the ISS measurement incrementally dosed gas into coal sample to several random pressure points and carried out in only a few studies to execute several isotherms for every piecemeal pressure step [11–14]. Higher requirements are put forward for either SSS or ISS measurement concerned with some recent developments of the mathematical modelling in dispersive diffusion behaviors [11–12] and swelling of coal induced by gas sorption [16–17], because accurately experimental data for the sorption rate of gas adsorption on coal is the necessary prerequisite to substantiate reliability of different adsorption models which are used to describe adsorption behavior of coal and insight into the mechanism of gas diffusion in coal.

Gibbsian surface excess adsorption [18] is increasingly being applied in many studies of gas adsorption on coal [1,7,9,11–14] to determine the rate of sorption and sorption capacity in volumetric sorption experiments, however in practice the GSE adsorption calculated using the real gas law is very sensitive to thermodynamic parameters. A number of studies on experimental accuracy of GSE adsorption have been reported in either SSS or ISS measurement from a thermodynamic perspective and summarized in this communication as follows. (1) Dependence of pressure. Blank tests as described by Li et al. [15] and Staib et al. [11–13] showed that pressure instability leads to difficulties in determining the initial pressure reading (the start point where the GSE data comes into effect [11,13]). (2) Dependence of temperature. Both Joule-Thomson expansion and the heat of sorption, found in the adsorption system similar to Fig. 1 by some researchers [15–17], leads

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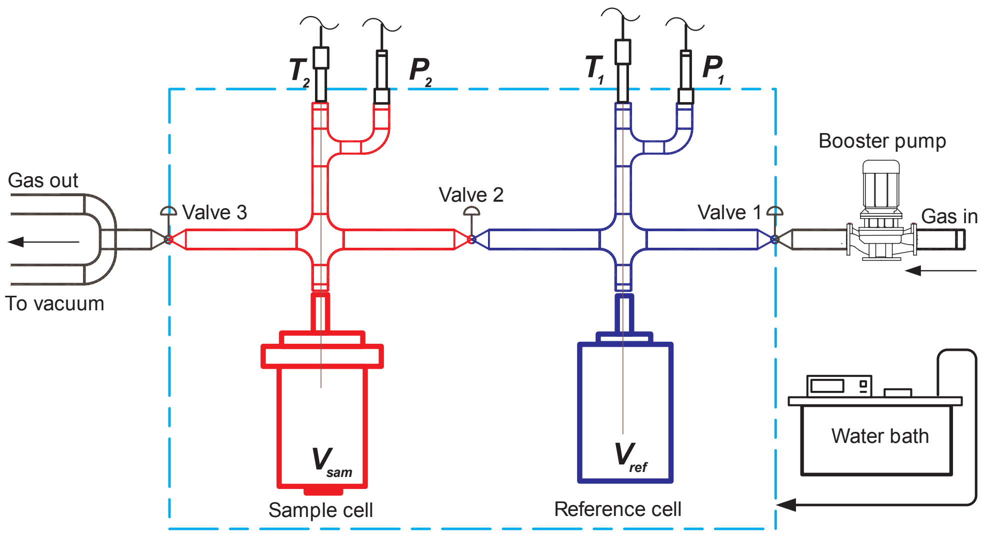

Fig. 1. Schematic experimental apparatus used for GSE adsorption test.

to an initial temperature fluctuations in the sorption process and also results in error in gas density calculations. (3) Dependence of volume. Sorption swelling behavior of coal sample [19] as well as sieving effect caused by Helium density method [19–21] easily results in volume uncertainty including the reference cell volume, the sample cell volume, the coal matrix volume and the void volume. The volume uncertainty had discussed in detail by Siemons et al. [19] and a solution of optimization procedure had been proposed, however, the effect of temperature and pressure on the GSE adsorption is usually determined through experimental screening and artificial selection. Staib et al. [11–13] recently reported a detailed GSE adsorption computing approach of the sorption rate for the ISS measurement, however, in their approaches only the sample cell (see Fig. 1) is chosen as an adsorption system and therefore uncertainty resulted from above-mentioned temperature and pressure fluctuations is inevitable in terms of artificial selection of invalid data period. Moreover, though the GSE theory has been often used in the SSS and ISS measurement, deep interpretation of GSE model for gas adsorption on coal has been given little attention.

In current work, a model analogous to GSE adsorption is presented for gas adsorption on heterogeneous coal particle. Based on this model, alternative method of gas adsorption rate calculations is developed to improve experimental accuracy for both SSS and ISS measurement taking into account both the sample cell and the reference cell in Fig. 1 as a whole adsorption system.

2. Modelling of gas adsorption on coal

The GSE model [18,22–23] provides a perfect solution for building an experimental system of interpreting and modelling sorption and diffusion of gas within the coal structure by means of measuring the practical thermodynamic parameters like pressure, temperature and volume to accurately obtain the sorption kinetic properties (such as the sorption rate, the amount of GSE gas and even actual adsorbed gas). Fig. 2 shows a picture of the basic principle of GSE model, and the Gibbs excess adsorption uptake (m^e) is often written as

$$m^e = m^a - v^a\rho \tag{1}$$

where v^a and m^a are, respectively, the volume of adsorbed phase and the actual amount of adsorbed phase in the adsorption system of Fig. 2; ρ is the density of free (non-adsorbed) gas under such an adsorption system. And therefore, The GSE (m^e) is the difference between the actual adsorption uptake (m^a) and the mass called the neglected part (m^n, see Fig. 2) that is equal to the free gas density (ρ) multiplied by the adsorbed-phase volume (v^a), this part (m^n) represents the amount of a gas that would be present in the adsorbed phase if the gas and the density of that phase is the same as those of the free gas. The m^n was elegantly subtracted/neglected by Gibbs from the actual adsorption uptake (m^a) to measure true experimental variable in his studies.

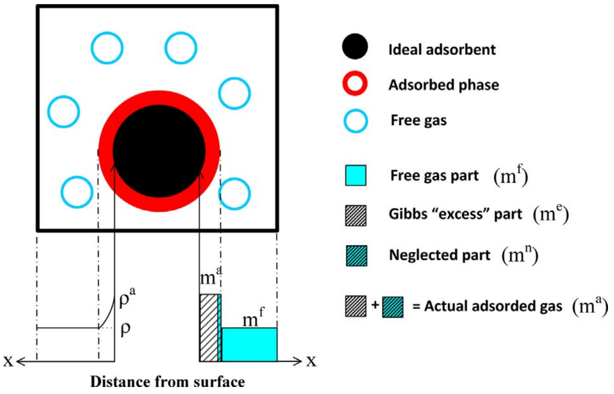

Fig. 2. Interpretation of the basic Gibbs model.

The basic Gibbs model is applied to gas adsorption on coal in many studies [1–15], and numerous laboratory experiments have demonstrated that coal as a special case of porous matrix has two classes of mechanisms: transport property and adsorption property. And thus, gas in coal under a Gibbs adsorption system of Fig. 2 may be present either in bulk form in larger pores (coarser pores and cleats) or in adsorbed form in smaller pores (nanoporous micropores).

To better understand the GSE sorption of gas on coal particle, Fig. 3 presents a GSE model of a heterogeneous coal particle, which has the generally accepted components including coal matrix and different types of pores (1, 2, 3, 4… k). And therefore, it can be further decomposed into a group of different adsorption sites (1, 2, 3, 4… k). When this coal particle under a GSE adsorption system (see Fig. 3) reaches in a sorption equilibrium with a given gas, According to the basic Gibbs model (Eq. (1)), the amount of GSE in a k type pore (m_k^e) can be expressed as

$$m_k^e = m_k^a - m_k^n = v_k\rho^a - v_k\rho \quad k = 1,2,... \tag{2}$$

where m_k^a and m_k^n are, respectively, the actual amount of absorbed phase and the neglected part (defined in Fig. 2) in the k-type pore; v_k is the adsorbed-phase volume in the k-type pore; ρ and ρ^a are, respectively, the density of free gas and the density of adsorbed phase in the k-type pore. Obviously, the total GSE of a given gas on the heterogeneous coal particle (m^e) can be a sum of its all pores and expressed as