Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

CH_4 and CO_2 adsorption measurement

Manometric gas adsorption analyzer is shown in Fig. 1s. It is composed of a stainless steel reference reservoir of known calibrated volume (determined by subtracting the weight of empty cylinder from the weight of the cylinder filled with water), sample holder, two electronic pressure transducers, discharge and vacuum outgassing lines, reduced dead-volume Swagelok valves and stainless steel tubing connected by Swagelok fitting.

The adsorbed amount is calculated from mass balance:

$$n_{ads} = n_1 + n_2 - n_3 = \frac{P_1 \cdot V_1}{z_1 \cdot R \cdot T_1} + \frac{P_2 \cdot V_d}{z_2 \cdot R \cdot T_2} - \frac{P_3 \cdot (V_1 + V_d)}{z_3 \cdot R \cdot T_3} \qquad (1s)$$

where n_1 is the amount of gas contained in the reservoir (V_1) before the injection into sample holder, n_2 – the amount of gas in the free space of sample holder (V_d) before the injection of the new dose, n_3 – the total (at equilibrium) amount of gas in the system (in gaseous phase) after opening the valve connecting the sample holder and the reservoir, n_{ads} – the adsorbed amount of gas, V_1 – volume of the reservoir, V_d – volume of the sample holder not occupied by the sample, z - gas compressibility coefficient depending on pressure and temperature (calculated from NIST database)[1], P and T – experimentally measured pressure and temperature at different steps of experiment. V_1 volume, employed for adsorbed amount calculation using (1s) is composed of the volumes of reference reservoir and tubing enclosed between valves 1, 2, 3, 4, 5 (measured by Helium expansion from reference reservoir).

The uncertainty of gas adsorption measurements was evaluated by error propagation in (1s) using the equation (2s):

$$\sigma^2_{n_{ads}} = \left(\frac{P_1/T_1}{z_1 \cdot R} - \frac{P_3/T_3}{z_3 \cdot R}\right)^2 \cdot \sigma^2_{V_1} + \left(\frac{P_2/T_2}{z_2 \cdot R} - \frac{P_3/T_3}{z_3 \cdot R}\right)^2 \cdot \sigma^2_{V_d} + \left(\frac{V_1}{z_1 \cdot R}\right)^2 \cdot \sigma^2_{P_1/T_1} + \left(\frac{V_m}{z_2 \cdot R}\right)^2 \cdot \sigma^2_{P_2/T_2}$$

$$+ \left(-\frac{V_1 + V_m}{z_3 \cdot R}\right)^2 \cdot \sigma^2_{P_3/T_3} \qquad (2s)$$

where σ_{V_1} – is the uncertainty of the reservoir volume measurement (0.1 cm^3), σ_{V_d} – the uncertainty of the sample holder volume measurement (deviation from an average of 5 measurements), and $\sigma_{P/T}$ – the uncertainty of P/T measurements provided by the equipment supplier (0.001 bar/°C).

(a) (b)

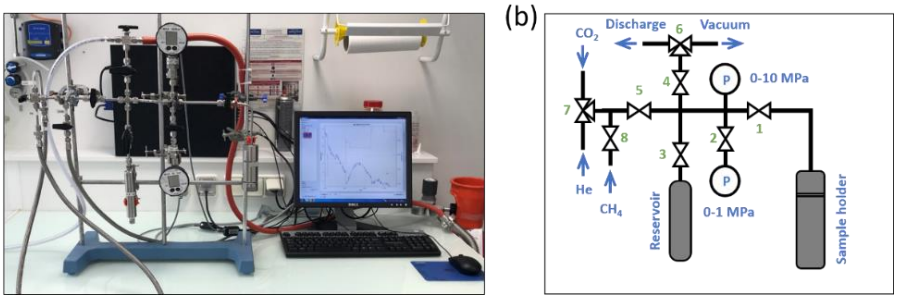

Fig. 1s. (a) photo and (b) schema of manometric gas adsorption analyzer.

1 E. W. Lemmon, I. H. Bell, M. L. Huber and M. O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.0, National Institute of Standards and Technology, 2018, 135.