Supplementary Materials for:

Optimized volume determinations and uncertainties for accurate and precise manometry

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Derivation of pressure deviations from ideality

Deviations from ideal gas behavior (PV = nRT) can be encapsulated by the compressibility factor, $Z = PV/nRT$, which is given by a series expansion in molar volume ($\bar{V} = V/n$) or pressure in the virial equation of state. This expansion is often truncated at the second term for gases under conditions of sufficiently low pressures and high temperatures without sacrificing precision (Poling et al. 2001) (Eq. (S-1)). The "second virial coefficient" (B(T)) in Eq. (S-1) is a characteristic property of the gas under consideration that depends on temperature T (Poling et al. 2001) (Figure S-1).

(S-1)
$$Z \approx 1 + B(T)\frac{P}{RT}$$
$$\text{or}$$
$$Z \approx 1 + B(T)\frac{n}{V}$$

Since the expected pressures of non-ideal gases can be calculated as $P_{VE} = nRTZ/V$, deviations from the pressures expected under the ideal gas law ($\Delta P = P_{VE} - P_{IGL}$) are approximately parabolic in the ideal gas law pressure (Eq. (S-2)).

(S-2)
$$\Delta P = \frac{nRT}{V}(Z-1) \approx \frac{B(T)}{RT}P_{IGL}^2$$

Accordingly, we demonstrate the range of ΔP's for He, N_2, CO_2, and dry air over pressures spanning 0 to 1000 Torr (main text, Figure 2) for an array of prescribed number of moles in a fixed cold-finger volume (V = 15 cm^3) at a typical laboratory temperature (T = 298.15 K). Uncertainty in pressures calculated with the virial equation stem directly from uncertainties in all measured values (P, V, T), and indirectly from T when choosing the appropriate value of B(T).

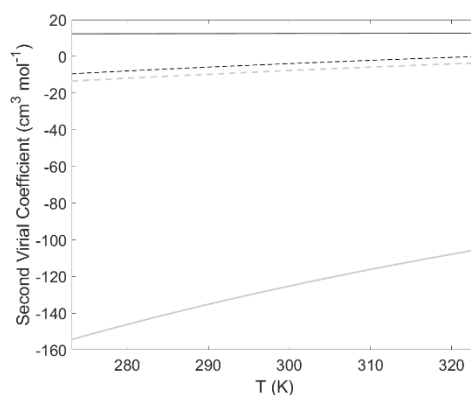**Figure S-1: Second Virial Coefficients, B(T),** as a function of temperature from 273.15 to 323.15 K for He (black solid line), N_2 (black dashed line), dry air (gray dashed line), and CO_2 (grey solid line). The curves were based on data and smoothing functions from the CRC Handbook of Chemistry and Physics (Rumble 2018) curves for He, N_2, and CO_2, and data from Sengers et al. (1971) for dry air.

Serial gas expansion method: derivation of V_1

In this method, equilibrium pressures (P_1, P_{12}, and P_{123}) and temperatures (T_1, T_{12}, and T_{123}) are measured during a series of gas expansions from the cold-finger (V_1) into successively larger volumes ($V_{12} = V_1 + V_2$, and $V_{123} = V_1 + V_2 + V_3$) that includes a clean, dry reference flask (V_3) whose volume was previously determined gravimetrically with pure water (*main text*, Figure 1). The number of moles of the gas (n) are conserved during the expansions, permitting calculation of V_1 from measurements of P_i's, T_i's, and V_3 using the appropriate equation of state, such as the ideal gas law or the virial equation. Despite the simplicity of this procedure, several potential errors must be considered.

First, the volumes defined above and in Figure 1 (main text) can change upon actuating valves A, B, C, and D. This error is most significant when using high-vacuum glass valves seated with an O-ring, but can be virtually eliminated if the manometric system and reference flask are constructed from lightly-greased tapered glass stopcocks (e.g., Chemglass Cat. No. CG-473) or similarly flat-seated metal valves. Henceforth, we shall assume the manometric systems under consideration were constructed with appropriate valves, rendering this error negligible.

Second, the capacitance diaphragm gauge (CDG) sensing element is a capacitor with one plate that deflects when pressurized. Thus, the volume contained by the manometer/cold-finger system (V_1) is not constant, but rather pressure-dependent. Consequently, the most general solution should quantify the volume of the cold-finger at the CDG equilibrium position (i.e., $V_{1,o}$ at $P = 0$ Torr) and parameterize the additional pressure-dependent volumes created when the diaphragm is deflected (ΔV_i is a function of P_i).

Third, as previously stated, deviations from ideal gas behavior can be detected for several gases in under typical conditions (main text, Figure 2) using the gauges studied here. Therefore, the most general and accurate set of equations describing the changes in pressure observed during serial gas expansion should correct for non-ideality (virial equation) and the pressure-dependent volumes generated by diaphragm deflections (e.g., $V_1 = V_{1,o} + \Delta V_1$):

(S-3)
$$V_{1,o} + \Delta V_1 = \frac{nRT_1}{P_1} Z_1$$

(S-4)
$$V_{12,o} + \Delta V_{12} = \frac{nRT_{12}}{P_{12}} Z_{12}$$

(S-5)
$$V_{123,o} + \Delta V_{123} = \frac{nRT_{123}}{P_{123}} Z_{123}$$

Since $V_{123,o} = V_{1,o} + V_2 + V_3$ and $V_{12,o} = V_{1,o} + V_2$, we can calculate $V_3 = V_{123,o} - V_{12,o}$ using equations (S-4) and (S-5).

$$(S\text{-}6) \qquad V_3 = \left(\frac{T_{123}}{P_{123}} Z_{123} - \frac{T_{12}}{P_{12}} Z_{12} \right) nR + (\Delta V_{12} - \Delta V_{123})$$

Solving this expressing for nR and substituting into Eq. (S-3) gives the most general expression for calculating $V_{1,o}$, the volume of the un-pressurized cold-finger flask, from the virial equation of state and measurements of temperature, pressure, and the volume of the reference flask (V_3).

$$(S\text{-}7) \qquad V_{1,o} = \frac{\frac{T_1}{P_1} Z_1}{\frac{T_{123}}{P_{123}} Z_{123} - \frac{T_{12}}{P_{12}} Z_{12}} \left(V_3 - (\Delta V_{12} - \Delta V_{123}) \right) - \Delta V_1$$

Rearranging Eq. (S-7) into Eq. (S-8) reveals three terms that can be considered.

$$(S\text{-}8) \qquad V_{1,o} = \left(\frac{\frac{T_1}{P_1} Z_1}{\frac{T_{123}}{P_{123}} Z_{123} - \frac{T_{12}}{P_{12}} Z_{12}} \right) V_3 - \left(\frac{\frac{T_1}{P_1} Z_1}{\frac{T_{123}}{P_{123}} Z_{123} - \frac{T_{12}}{P_{12}} Z_{12}} \right) (\Delta V_{12} - \Delta V_{123}) - \Delta V_1$$

The first term on the right-hand side of Eq. (S-8) is the volume that would be calculated assuming the additional volumes due to CDG diaphragm deflections are negligible. The second term corrects this for CDG deflection volumes (ΔV_{12} and ΔV_{123}) associated with measuring P_{12} and P_{123}. The final term corrects for the CDG deflection volume associated with the initial pressure measurement. This is the largest correction because the pressures and deflection volumes decrease with each gas expansion. If ignoring these corrections yields significant errors, then the deflection volumes can be parameterized as directly proportional to P (e.g., Eq. (S-31), derived below). Otherwise, Eq. (S-7) can be simplified as follows:

First, the maximum volume change at full scale deflection for the CDGs studied here is ~0.03 cm^3 (Dick Jacobs, Principle Applications Engineer, MKS Instruments, Inc., personal communication). This induces a maximum relative error that is similar in magnitude to the minimum relative uncertainty simulated for an optimized system with a 15 cm^3 cold-finger (~0.002). Since P_1, P_{12}, and P_{123} are lower than the upper detection limit of the gauge, the error due to deflection volumes will be within measurement uncertainty. Therefore, the deflection volumes may be assumed negligible for cold-finger volumes greater than or equal to ~15 cm^3 connected to comparable CDG's (Eq. (S-9)).

$$(S\text{-}9) \qquad V_1 \approx \frac{\frac{T_1}{P_1} Z_1}{\frac{T_{123}}{P_{123}} Z_{123} - \frac{T_{12}}{P_{12}} Z_{12}} V_3$$

Second, if the ambient temperature is constant ($T_1 \approx T_{12} \approx T_{123}$) during the determination of V_1, then the Virial coefficient terms cancel from the denominator (Eq. (S-10)).

$$(S\text{-}10) \qquad V_1 \approx \frac{\dfrac{1}{P_1}}{\dfrac{1}{P_{123}} - \dfrac{1}{P_{12}}} V_3 Z_1$$

Finally, if the calibration gas does not deviate significantly from ideality over the range of measured pressures ($\Delta P \leqslant$ gauge increment), then it may be treated as an ideal gas ($Z \equiv 1$). In that case, the expression would reduce to a form derived from Boyle's law.

Serial gas expansion method: propagation of uncertainties

If deflection volumes and deviations from ideal gas behavior are negligible, then the cold-finger volume (V_1) can be determined via the reference flask volume (V_3) and the equilibrium pressure readings (P_i's) as shown in Eq. (S-10). Consequently, the uncertainty of V_1 can be estimated by propagating uncertainties from V_3 and the P_i's through linearized Taylor Series expansions, where σ_{P_1}, $\sigma_{P_{12}}$, $\sigma_{P_{123}}$, and σ_{V_3} are single standard deviations of P_1, P_{12}, P_{123}, and V_3, respectively, and $\sigma_{P_1 P_{12}}$, $\sigma_{P_1 P_{123}}$, $\sigma_{P_1 V_3}$, $\sigma_{P_{12} P_{123}}$, $\sigma_{P_{12} V_3}$, and $\sigma_{P_{123} V_3}$ are the covariances of P_1 and P_{12}, P_1 and P_{123}, P_1 and V_3, P_{12} and P_{123}, P_{12} and V_3, and P_{123} and V_3, respectively.

$$(S\text{-}11) \qquad \sigma V_1 = \left[\begin{array}{l} \left(\dfrac{\partial V_1}{\partial P_1}\sigma_{P_1}\right)^2 + \left(\dfrac{\partial V_1}{\partial P_{12}}\sigma_{P_{12}}\right)^2 + \left(\dfrac{\partial V_1}{\partial P_{123}}\sigma_{P_{123}}\right)^2 + \left(\dfrac{\partial V_1}{\partial V_3}\sigma_{V_3}\right)^2 \\[4mm] +2\left(\begin{array}{l} \dfrac{\partial V_1}{\partial P_1}\dfrac{\partial V_1}{\partial P_{12}}\sigma_{P_1 P_{12}} + \dfrac{\partial V_1}{\partial P_1}\dfrac{\partial V_1}{\partial P_{123}}\sigma_{P_1 P_{123}} + \dfrac{\partial V_1}{\partial P_1}\dfrac{\partial V_1}{\partial V_3}\sigma_{P_1 V_3} + \\[4mm] \dfrac{\partial V_1}{\partial P_{12}}\dfrac{\partial V_1}{\partial P_{123}}\sigma_{P_{12} P_{123}} + \dfrac{\partial V_1}{\partial P_{12}}\dfrac{\partial V_1}{\partial V_3}\sigma_{P_{12} V_3} + \dfrac{\partial V_1}{\partial P_{123}}\dfrac{\partial V_1}{\partial V_3}\sigma_{P_{123} V_3} \end{array} \right) \end{array} \right]^{1/2}$$

This expression was simplified and used to estimate the relative uncertainty of V_1 as follows.

First, numerical simulations of gas expansions demonstrated that the covariances shown in Eq. (S-11) contributed negligible uncertainty and were ignored hereafter.

Second, the reference flask's volume (V_3) was assumed to have been previously measured gravimetrically based on temperature (T), density (ρ_{water}), and buoyancy corrected mass (m_3) of pure, degassed water (Eq. S-12) (Harris 2018). The relative uncertainty of V_3 was approximately equal to the relative uncertainty of m_3 (Eq. (S-13)), assuming the contributions from the uncertainties of density and temperature were negligible compared to that from mass.

(S-12)
$$V_3 = \frac{m_3}{\rho_{water}}$$

(S-13)
$$\frac{\sigma_{V_3}}{V_3} = \sqrt{\left(\frac{\sigma_{m_3}}{m_3}\right)^2 + \left(\frac{\sigma_{\rho_{water}}}{\rho_{water}}\right)^2 + \left(\frac{\sigma_T}{\rho_{water}}\frac{\partial\rho_{water}}{\partial T}\right)^2} \approx \frac{\sigma_{m_3}}{m_3}$$

Third, the partial derivatives of V_1 were expressed as functions of V_1:

(S-14)
$$\frac{\partial V_1}{\partial P_1} = -\frac{V_1}{P_1}$$

(S-15)
$$\frac{\partial V_1}{\partial P_{12}} = -\frac{V_1}{P_{12}}\left(\frac{1}{P_{123}} - \frac{1}{P_{12}}\right)^{-1}$$

(S-16)
$$\frac{\partial V_1}{\partial P_{123}} = \frac{V_1}{P_{123}}\left(\frac{1}{P_{123}} - \frac{1}{P_{12}}\right)^{-1}$$

(S-17)
$$\frac{\partial V_1}{\partial V_3} = \frac{V_1}{V_3}$$

Substituting Eq. (S-13) - (S-17) into Eq (S-11), ignoring the covariance terms, and rearranging, yielded a simplified expression for the relative uncertainty of V_1 (Eq. (S-18)).

(S-18)
$$\frac{\sigma_{V_1}}{V_1} \approx \sqrt{\left(\frac{\sigma_{P_1}}{P_1}\right)^2 + \left(\frac{1}{P_{123}} - \frac{1}{P_{12}}\right)^{-2}\left[\left(\frac{\sigma_{P_{12}}}{P_{12}}\right)^2 + \left(\frac{\sigma_{P_{123}}}{P_{123}}\right)^2\right] + \left(\frac{\sigma_{m_3}}{m_3}\right)^2}$$

Cryogenic transfer method: derivation of V_1

In the cryogenic transfer method, a dry condensable gas (e.g. CO_2) is directly and completely transferred from the reference flask (V_3) to the cold-finger (V_1) using a cryogenic bath (main text, Figure 1). First, the system is filled with a quantity of CO_2 and then the initial pressure and temperature are measured (P_3, T_3). Next, the gas in the reference flask (V_3) is isolated (P_3), while cold-finger (V_1) and corridor (V_2) are evacuated. Finally, the gas in V_3 is cryogenically transferred into V_1, the cold-finger is warmed, and the final pressure and temperature are measured (P_1, T_1). Since this method relies upon a condensable gas, it requires a real equation of

state for greatest accuracy. If volume changes caused by the diaphragm deflection (ΔV_1) are also considered, then $V_{1,o}$ and V_3 can be expressed as functions of n, R, T_i, P_i, and Z_i using the virial equation of state.

(S-19)
$$V_{1,o} + \Delta V_1 = \frac{nRT_1}{P_1} Z_1$$

(S-20)
$$V_3 = \frac{nRT_3}{P_3} Z_3$$

$V_{1,o}$ can be calculated by solving Eq. (S-20) for nR and substituting into Eq. (S-19).

(S-21)
$$V_{1,o} = \frac{P_3 T_1 Z_1}{P_1 T_3 Z_3} V_3 - \Delta V_1$$

The correction for CDG diaphragm deflection ($-\Delta V_1$) can be safely neglected for sufficiently large cold-fingers and low pressures. Furthermore, if $T_1 \approx T_3$, then V_1 can be calculated with Eq. (S-22).

(S-22)
$$V_1 = \frac{P_3 Z_1}{P_1 Z_3} V_3$$

Lastly, if the gas follows ideal behavior ($Z_1 = Z_2 = 1$) over the range of observed temperatures and pressures, then Eq. (S-22) reduces to Boyle's Law.

Cryogenic transfer method: propagation of uncertainties

The uncertainty of V_1 via cryogenic transfer (Eq.(S-22)) can be estimated by propagating the uncertainties of V_3 and the P_i's through linearlized Taylor Series expansions, where σ_{P_1}, σ_{P_3}, σ_{V_3} are the single standard deviations of P_1, P_3, and V_3, and the terms $\sigma_{P_1 P_3}$, $\sigma_{P_1 V_3}$, and $\sigma_{P_3 V_3}$ are the covariances of P_1 and P_3, P_1 and V_3, and P_3 and V_3, respectively.

(S-23)
$$\sigma V_1 = \sqrt{ \left(\frac{\partial V_1}{\partial P_1} \sigma_{P_1} \right)^2 + \left(\frac{\partial V_1}{\partial P_3} \sigma_{P_3} \right)^2 + \left(\frac{\partial V_1}{\partial V_3} \sigma_{V_3} \right)^2 + 2 \left(\frac{\partial V_1}{\partial P_1} \frac{\partial V_1}{\partial P_3} \sigma_{P_1 P_3} + \frac{\partial V_1}{\partial P_1} \frac{\partial V_1}{\partial V_3} \sigma_{P_1 V_3} + \frac{\partial V_1}{\partial P_3} \frac{\partial V_1}{\partial V_3} \sigma_{P_3 V_3} \right) }$$

As with the serial gas expansion method, covariances calculated from numerical simulations contributed negligible uncertainty and were ignored hereafter.

The partial derivatives of V_1 were expressed as functions of V_1 (Eq. (S-24) - (S-26)).

(S-24)
$$\frac{\partial V_1}{\partial P_1} = \frac{-V_1}{P_1 Z_1}$$

(S-25)
$$\frac{\partial V_1}{\partial P_3} = \frac{V_1}{P_3 Z_3}$$

(S-26)
$$\frac{\partial V_1}{\partial V_3} = \frac{V_1}{V_3}$$

Substituting Eq. (S-13) and Eq. (S-24) through (S-26) into Eq. (S-23), ignoring the covariance terms, and rearranging, gave a simplified expression for the relative uncertainty of V_1 (Eq. (S-27)).

(S-27)
$$\frac{\sigma_{V_1}}{V_1} = \sqrt{\frac{1}{Z_1^2}\left(\frac{\sigma_{P_1}}{P_1}\right)^2 + \frac{1}{Z_3^2}\left(\frac{\sigma_{P_3}}{P_3}\right)^2 + \left(\frac{\sigma_{m_3}}{m_3}\right)^2}$$

The relative uncertainty of V_1 measured by the cryogenic transfer method is minimized and essentially constant when it is determined with pressures that fall between P_{cusp} and $P_{full\ scale}$. This property results from the following. First, the relative uncertainty of V_3 (i.e., σ_{m3}/m_3) may be taken as a constant for any given reference flask. Second, the relative uncertainties of P_1 and P_2 are also constant for pressures between P_{cusp} and the CDG full scale pressure (i.e., 6.67 to 100 Torr or 66.7 to 1000 Torr on the gauges studied here). Finally, the CO_2 compressibility factor changes by $\leqslant$ *ca.* 0.7 % from 0 to 1000 Torr (Figure S-2), rendering the squared compressibility factors of CO_2 in Eq. (S-27) nearly constant (e.g., $Z = 0.9996$ to 0.9932 for $P = 66.7{\sim}999.9$ Torr).
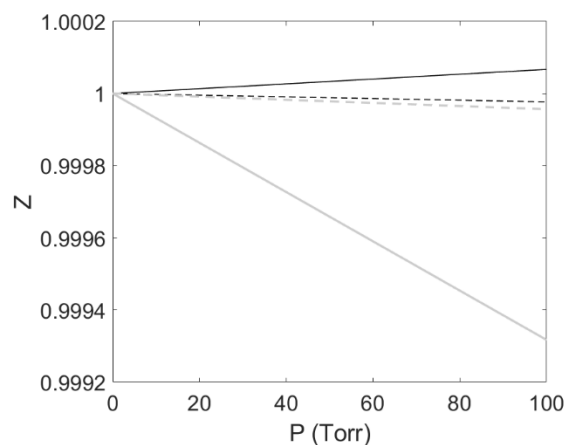

Figure S-2: Compressibility factors (Z) of He (black solid line), N_2 (black dashed line), Dry air (gray dashed line), and CO_2 (grey solid line) from 0 to 1000 Torr at 298.15 K. Values were calculated with B(T)'s of 12.44 cm^3 mol^{-1}, -4.3 cm^3 mol^{-1}, -127 cm^3 mol^{-1} and -8.0885 cm^3 mol^{-1} for He, N_2, CO_2, and dry air, respectively (Figure S-1).

CDG deflection volume parameterization

As mentioned above, CDG diaphragm deflections increase the volume of the manometer system and the uncertainty of V_1 determinations. To quantify the volume changes caused by diaphragm deflections, we first assume that deflections in the center of the diaphragm (h) can be calculated by Eq. (S-28), where P is pressure, v is the Poisson ratio, E is the Young modulus, t is the thickness of the diaphragm, and a is the free radius of the diaphragm (Jousten and Naef 2011).

(S-28)
$$h = \frac{3a^4(1 - v^2)}{16Et^3} P$$

The deflection height h is an approximately linear function of P because a, v, E, and t are nearly constant over the range of commonly observed pressures. If we assume that the diaphragm deflects as a spherical cap, then the volume change due to the deflection can be expressed as a function of h (Eq. (S-29)).

(S-29)
$$\Delta V = \frac{1}{6}\pi h(3a^2 + h^2)$$

The first derivative of ΔV with respect to h is given by Eq. (S-30).

(S-30)
$$\frac{d\Delta V}{dh} = \frac{\pi}{2}(a^2 + h^2) \approx \frac{\pi}{2}a^2$$

Normally, the free radius of the diaphragm is much larger than the deflection at its center from the zero position, hence dΔV/dh is approximately constant at $0.5\pi a^2$; in other words, ΔV is practically proportional to h over the range of measurable pressures, and thus directly proportional to P via Eq. (S-28). Since the maximum deflection volume of our chosen gauge is given by the manufacturer as $\Delta V_{max} = 0.03$ cm^3 at full scale pressure (e.g., at $P_{max} = 100$ Torr; personal communication) and the minimum deflection volume $\Delta V_{min} = 0$ at $P_{min} = 0$, then ΔV at any measured P can be estimated via Eq. (S-31).

(S-31)
$$\Delta V \approx \frac{\Delta V_{max}}{P_{max}} P$$

Quality control of numerical simulation results

In this work, the standard deviations and relative uncertainties of V_1 in all numerical simulations were calculated assuming the simulated results of V_1 were normally distributed. This assumption was checked by the "normplot" command in MATLAB, which generated normal probability plots for arrays of our simulated data. The numerically simulated V_1 measurements by serial gas

expansion and cryogenic transfer methods consistently fell on the normal probability line (Figure S-3) with minor deviations on the wings. This indicates that uncertainties on V_1 are largely symmetric and can be treated as single standard deviations of normally distributed data during subsequent manometric measurements.
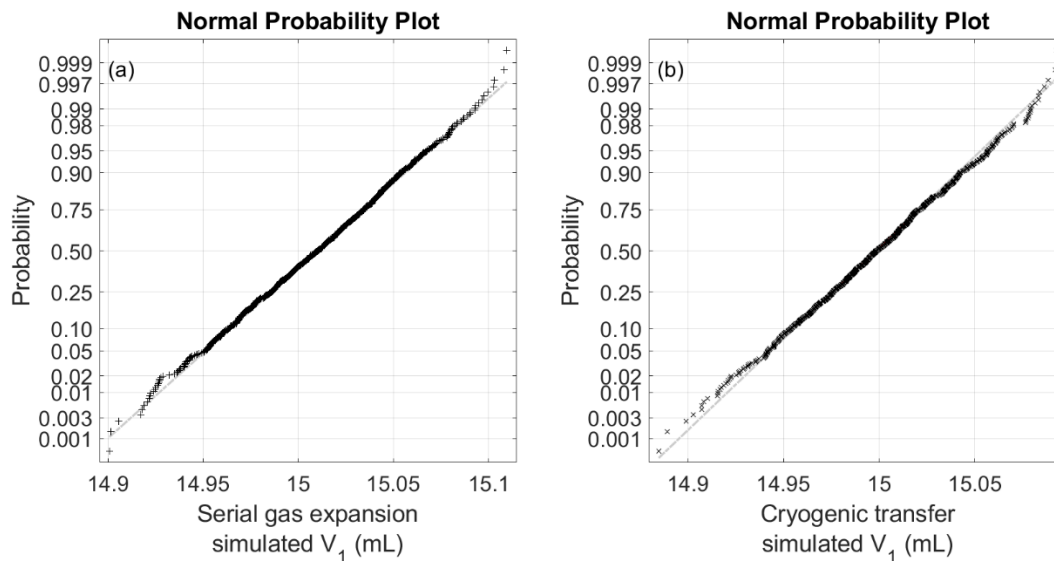

Figure S-3: Example normal probability plots of V_1 (mean = 15 cm^3) determined by numerical simulations of the (a) serial gas expansion and (b) cryogenic transfer methods for V_2 = 5 cm^3, V_3 = 153.1 cm^3, T = 298.15 K, at optimized compression ratios and initial pressures. Light grey dashed lines represent perfectly normal distributions.

Supplementary Materials References

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MATLAB Code: Numerical simulation of $\sigma V_1/V_1$ for serial gas expansion method

```
% Title:
% Manometer calibration simulation: with corridor (V2>=0)

% Subtitle:
% A simple script to find the optimum flask size (V3) for the highest
% precision measurements of the volume of a manometer's cold finger (V1)

% Xi Lu / Steven R. Beaupre
% Stony Brook University
% Created: 20170927
% Edited: 20180717

% Description:
% This program simulates measurements of pressure drops when expanding gas
% from an unknown volume (V1, the cold finger) into a flask of known volume (V3)
% with an intermediate corridor of known volume (V2). Those pressure drops are then
% used to calculate the volume (V1) via Virial equation (NOT ideal gas law),
% assuming the temperature (T), and associated virial coefficients, are constant:

% P*V = n*Z*R*T, where Z ~= 1+B*(P/(R*T)), and B = 2nd virial coefficient for a chosen gas at temperature T

% The program simulates many (n) serial gas expansions for a range of manometric systems, where
% each system is defined by its cold finger, corridor, and reference flask volumes (V1, V2, V3).

% P1*V1= n*R*T*(1+B*(P1/(R*T)))
% P12*V12= n*R*T*(1+B*(P12/(R*T)))
% P123*V123= n*R*T*(1+B*(P123/(R*T)))

% where

% V12 = V1 + V2
% V123 = V1 + V2 +V3
% V1 = cold finger volume
% V2 = corridor volume
% V3 = calibration flask volume
% P1 = pressure measured inside V1 before expansion
% P12 = pressure measured after expanding into V1 + V2 =V12
% P123 = pressure measured after expanding into V1 + V2+ V3 = V123
% n = the mole number of gas molecules originally kept in the cold finger (as n_mol in the script)
% R, B= constants (R is presented as R_g in the script)

% It then calculates the average and standard deviation of V1 for all n simulations and systems,
% then searches for the values of total volume (V2 + V3) that yields the lowest relative uncertainty
% (std dev V1 / V1) of the cold finger volume.
% The program also simulates multiple V1 to seek the underlying trend of optimum V3/V1.

% --------------------------------------------------------------------------------------------------------------------------

% Constants:
% % These constants can be adjusted according to the actual conditions of users
R_g = 62363.7;              % universal gas constant (mL Torr. mol-1 K-1)
```

```
B = -8.0885;            % Second virial coefficients of dry air (mL*mol^-1) (at 298.15K)
T = 298.15;             % ambient temperature (K)
Minc = 0.1;             % increment of balance mass (g)
Pinc = 0.01;            % increment on pressure gauge, e.g., Baratron CDG (Torr)
ruP = 0.0015;           % relative uncertainty on pressure measurements
dH2O = 0.9970470;       % density of water under T = 298.15K (g/mL)
sV3 = Minc/dH2O;        % standard deviation (uncertainty) on V3 (mL)
P1fix = 76;             % approximate (or designed) initial pressure in cold finger (Torr.)
V1min = 1;              % minimum cold finger size investigated in this program (mL)
V1max = 31;             % maximum cold finger size investigated in this program (mL)
V1inc = 1;              % increment between adjacent cold finger size investigated in this program (mL)
V2min = 0;              % minimum corridor size tested in this program (mL)
V2max = 49;             % maximum corridor size tested in this program (mL)
V2inc = 1;              % increment between adjacent corridor size tested in this program (mL)
V3min = 0.1;            % minimum flask size tested in this program (mL)
V3max = 500.1;          % maximum flask size tested in this program (mL)
V3inc = 0.5;            % increment between adjacent flask sizes tested in this program (mL)
n = 1000;               %number of simulations (cases) for each V1+V2+V3 combination

% Vectors of manometric systems:
V1 = (V1min:V1inc:V1max)';      % different cold finger sizes (mL)
V2 = (V2min:V2inc:V2max)';      % different corridor sizes (mL)
V3 = (V3min:V3inc:V3max)';      % different flask sizes (mL)
n_mol = P1fix*V1./(R_g*T);      % estimate the mole number of gas molecules originally kept in the cold finger
                                % via P1fix, V1 and ideal gas law (functions as constant in later calculations)


% % preallocate vectors of exact values.
P1 = ones(length(V1),1);   % will hold P1 calculated exactly from each n_mol and V1 via Virial equation
sP1 = ones(length(V1),1);  % will hold standard deviation of each P1
optV23 = ones(length(V1),1); % will hold the optimum V2+V3 for each of the various V1
optP123 = ones(length(V1),1); % will hold the optimum P123 calculated from the optimum optCR

% % Preallocate vector of values simulated with uncertainties
V1sim = ones(n,1);
V2sim = ones(n,1);
V3sim = ones(n,1);
P1sim = ones(n,1);
P12sim=ones(n,1);
P123sim=ones(n,1);

% %  preallocate matrices of exact values
V12 = ones(length(V2), length(V1));                 % will hold the V12 calculated via V1+V2
V123 = ones(length(V2), length(V1), length(V3));    % will hold the ideal V123 calculated via V1+V2+V3
P12 = ones(length(V2), length(V1));                 % will hold the ideal P12 calculated via Virial equation
P123 = ones(length(V2), length(V1), length(V3));    % will hold the ideal P123 calculated via Virial equation
sP12 = ones(length(V2), length(V1));                % will hold standard deviation of each P12
sP123 = ones(length(V2), length(V1), length(V3));   % will hold standard deviation of each P123

% % Preallocate matrices of mean values, standard deviations, and optimum values calculated from simulations with
% % uncertainties for each combination of V1, V2, and V3

mV3sim = ones(length(V2), length(V1), length(V3));      % means of simulated V3
mP1sim = ones(length(V2), length(V1), length(V3));      % means of simulated P1
mP12sim = ones(length(V2), length(V1), length(V3));     % means of simulated P13
mP123sim = ones(length(V2), length(V1), length(V3));    % means of simulated P123
mV1sim = ones(length(V2), length(V1), length(V3));      % means of calculated V1
```

```
sV1sim = ones(length(V2), length(V1), length(V3));          % standard deviation of calculated V1
ruV1sim = ones(length(V2), length(V1), length(V3));         % relative uncertainty of calculated V1

optV2 = ones(1, length(V1), length(V3));          % optimum V2 for each of the various V1+V3 combinations
optCR_V2 = ones(1, length(V1), length(V3));       % optimum V2/V1 for each V1+V3 combinations
optV3 = ones(length(V2),length(V1));              % optimum V3 for each of the various V1+V2 combinations
optCR_V3 = ones(length(V2),length(V1));           % optimum V3/V1 for each V1+V2 combinations


% --------------------------------------------------------------------------------------------------------------------------

% Simulation:

% % Calculate exact values of all expansion volumes (V12 = V1 + V2,  V123 = V1 + V2 + V3)
for i = 1 : length(V1)
    V12(: ,i) = V1(i,1)+V2;
    for k = 1 : length(V3)                         % calculate the exact values of V123 and P123
        V123(:, :, k) = V12+V3(k,1);
    end

    %  % Calculate P1, P12 and P123 via Virial equation, also estimate their uncertainty

    P1(i, 1) = VirialGL(n_mol(i,1), V1(i,1), T, B);     % calculate P1 via Virial equation (Torr)
    tsP1 = P1(i,1)*ruP;                                 % calculate the uncertainty of P1
    if tsP1 >= Pinc
        sP1(i,1) = tsP1;     % if the uncertainty of P1 calculated by the tsP1 equation is larger than increment of the
                             % pressure gauge, the result (tsP13) represent the uncertainty of P1 measurements
    else
        sP1(i,1) = Pinc;                % Otherwise the increment of pressure gauge determines the uncertainty
                                        % of P1 measurement
    end

    for j = 1 : length(V2)                          % loop for each V1+V2 combination
        P12(j ,i) = VirialGL(n_mol(i,1), V12(j, i), T, B); % calculate P12 via Viral equation (Torr)
        tsP12 = P12(j,i)*ruP;                       % calculate the uncertainty on P12
        if tsP12 >= Pinc
            sP12(j,i) = tsP12;   % if the uncertainty of P12 calculated by the tsP12 equation is larger than increment of
                                 % the pressure gauge, the result (tsP12) represent the uncertainty of P12 measurements
        else
            sP12(j,i) = Pinc;               % Otherwise the increment of pressure gauge determines the uncertainty
                                            % of P12 measurement
        end

        for k = 1 : length(V3)                              % loop for each V1+V2+V3 combination
            P123(j,i,k) = VirialGL(n_mol(i,1), V123(j,i,k), T, B);  % calculate P123 via Virial equation (Torr)
            tsP123 = P123(j,i,k)*ruP;                       % calculate the uncertainty on P123
        if tsP123 >= Pinc
            sP123(j,i,k) = tsP123;        % if the uncertainty of P123 calculated by the tsP123 equation is larger than
                                          % increment of the pressure gauge, the result (tsP123) represent the uncertainty
                                          % of P123 measurements
        else
            sP123(j,i,k) = Pinc;          % Otherwise the increment of pressure gauge determines the uncertainty
                                          % of P123 measurement
        end

    % % The n different simulations for each case
```

```
        V3sim = normrnd(V3(k,1), sV3, n, 1);              % simulate variability in V3, as if each determination were
                                                          % performed with a different measurement of the same
                                                          % reference flask's volume
        P1sim = normrnd(P1(i,1), sP1(i,1), n, 1);              % simulate the P1 measurement with uncertainty
        P12sim = normrnd(P12(j,i), sP12(j,i), n, 1);          % simulate the P12 measurement with uncertainty
        P123sim = normrnd(P123(j,i,k), sP123(j,i,k), n, 1);   % simulate the P123 measurement with uncertainty

        % Calculate mean values of simulated V3, P1, P12, and P123
        mV3sim(j,i,k) = mean(V3sim);
        mP1sim(j,i,k) = mean(P1sim);
        mP12sim(j,i,k) = mean(P12sim);
        mP123sim(j,i,k) = mean(P123sim);

% Calculate V1 from simulated pressure measurements and simulated V3
        V1sim = ((P1sim.*P12sim.*P123sim.*V3sim.*B) +
(P12sim.*P123sim.*V3sim.*R_g.*T))./(P1sim.*(P12sim - P123sim).*R_g.*T);

        mV1sim(j,i,k) = mean(V1sim);                       % mean of calculated V1
        sV1sim(j,i,k) = std(V1sim);                        % standard deviation of calculated V1
        ruV1sim(j,i,k) = sV1sim(j,i,k)/V1(i,1);            % relative uncertainty of calculated V1
    end
  end
end


% find optimum values

% % find the minimum relative uncertainties of V1
[minruV1sim_V2, optj] = min(ruV1sim,[],1);                 % minimum relative uncertainties with respect to V2
[minruV1sim_V3, optk] = min(ruV1sim,[],3);                 % minimum relative uncertainties with respect to V3
[minruV1sim, finoptj] = min(minruV1sim_V3,[],1);           % minimum relative uncertainties with respect to V2 and V3
minruV1sim = minruV1sim';                                  % transpose minimum relative uncertainty of V1 vector for
future calculations

% % Search for values of V2 and V3 that correspond to the minimum relative uncertainties of V1 calculated above
for i = 1 : length(V1)
  for k = 1 : length(V3)                                   % find the optimum V2
optV2(1,i,k) = V123(optj(1,i,k),i,k)-V1(i,1)-V3(k,1);      % find the matrix of optimum V2 which render the
                                                          % most precise measurement for the given V1+V3
                                                          % combination
        optCR_V2(1,i,k) = optV2(1,i,k)/V1(i,1);           % find the matrix of optimum V2/V1 ratios
  end

  for j = 1 : length(V2)                                   % find the optimum V3
        optV3(j,i) = V123(j,i,optk(j,i))-V1(i,1)-V2(j,1);  % find the matrix of optimum V3 which render the
                                                          % most precise measurement for the given V1+V2
                                                          % combination
        optCR_V3(j,i) = optV3(j,i)/V1(i,1);               % find the matrix of optimum V3/V1 ratios
  end

    optV23(i,1)=V123(finoptj(1,i),i,optk(finoptj(1,i),i))-V1(i,1);      % find the optimum V2+V3 which render
                                                          % the most precise measurement for each
                                                          % given V1

    optP123(i,1)=P123(finoptj(1,i),i,optk(finoptj(1,i),i));            % find the optimum P123 which render the
                                                          % most precise measurement foreach given
                                                          % V1
```

end

```
 optCR = optV23./V1;                                    % calculate the optimum compression ratio ((V2+V3)/V1)


% Figures
fs = 20; % font size

figure;
subplot(1,2,1); BubblePlot(V1,optCR,minruV1sim,'k');
xlabel('V_1 (mL)','fontSize',fs), ylabel('Optimum (V2+V3)/V1','fontSize',fs);
legend('Size: min. relative uncertainty of V1');
set(gca,'fontSize',fs)
subplot(1,2,2); plot(V1,minruV1sim, 'k')
xlabel('V_1 (mL)','fontSize',fs), ylabel('min. relative uncertainty of V1','fontSize',fs);
set(gca,'fontSize',fs)

% % to compare the relative uncertainty of V1 achieved over full range of tested V3 for V1 of 5, 15 and 25 mL
minruV1sim_test_1 (:,1) = minruV1sim_V2(1,5,:);
minruV1sim_test_2 (:,1) = minruV1sim_V2(1,15,:);
minruV1sim_test_3 (:,1) = minruV1sim_V2(1,25,:);

figure;
subplot(1,3,1);
scatter(V3, minruV1sim_test_1, 'k');
xlabel('V_3 (mL)','fontSize',fs), ylabel('min. \sigma V_1/V_1','fontSize',fs);
set(gca,'fontSize',fs)
subplot(1,3,2);
scatter(V3, minruV1sim_test_2, 'k');
xlabel('V_3 (mL)','fontSize',fs), ylabel('min. \sigma V_1/V_1','fontSize',fs);
set(gca,'fontSize',fs)
subplot(1,3,3);
scatter(V3, minruV1sim_test_3, 'k');
xlabel('V_3 (mL)','fontSize',fs), ylabel('min. \sigma V_1/V_1','fontSize',fs);
set(gca,'fontSize',fs)
```

MATLAB Code: VirialGL function

```
function P_Virial = VirialGL(n,V,T,B)
% Description:
% VirialGL(n,V,T, B) is a function applied to calculate non-ideal gas pressure P with the Virial equation.
% Results are calculated based on mole number of gas molecules (n), volume occupied by the gas
% (V), temperature of the gas (T), AND the second Virial coefficient of gas (B)

% created by Xi Lu, 20180118
% edited: 20180717

% The Virial equation:
% % P*V = n*Z*R*T
% Z ~= 1+B*(P/(R*T))
% Thus, P_Virial = n*R*T/(V-(n*B))

% input units
% n: mol
% V: mL
% T: K
% B: mL mol^-1

% output units: Torr

% define constants
R_g = 62363.7; % gas constant (mL Torr. mol-1 K-1)

% calculation
P_Virial = n*R_g*T/(V-(n*B));
```