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Effect of Temperature on Adsorption Behavior of Alumina from Two Binary Liquid Mixtures

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Composite adsorption isotherms of cyclohexane–benzene and benzene–dioxane mixtures on alumina at 20, 30, and 40 °C have been determined. The adsorption data have been used for calculating the surface activity coefficients at different temperatures, and from the latter the excess surface entropy values have been derived.

Adsorption behavior of several binary solutions on alumina and silica surfaces has been investigated extensively in the past but these studies have been devoted either to the estimation of surface area or to finding out the preferential adsorption of one of the components of the mixture on the solid (*1–4*). In most of these studies, the adsorption measurement had generally been made at one temperature only. It was, therefore, considered worthwhile to determine adsorption data at three temperatures and examine the effect of temperature on the adsorption behavior. The two mixtures chosen for this study are benzene–cyclohexane and benzene–dioxane. These systems have been used extensively for evaluation of various thermodynamic properties in recent studies (*5–8*). Though these solutions do not exhibit ideal solution behavior, the deviation from such character is not significant. In fact, the use of equations derived for ideal solutions can indicate the nonideal characteristics of a binary solution. The adsorption data have been employed to calculate the surface activity coefficients, and from the latter the surface entropy parameters have been derived.

Theory

Writing the thermodynamic potentials of the components in the surface phase (σ) and the bulk phase (l) and equating the two at equilibrium with appropriate standard states, one can show that

$$\gamma_i = \frac{A_i}{\bar{A}_i}\gamma_i + \frac{RT}{\bar{A}_i}\ln\frac{a_i^{\sigma}}{a_i^{l}} \tag{1}$$

$$= \frac{A_j}{\bar{A}_j}\gamma_j + \frac{RT}{\bar{A}_j}\ln\frac{a_j^{\sigma}}{a_j^{l}} \tag{2}$$

After suitable rearrangement of the above equations it follows that

$$\frac{a_j^{\sigma}}{a_j^{l}} = \left(\frac{a_i^{\sigma}}{a_i^{l}}\right)^{\bar{A}_j/\bar{A}_i} \exp\left[\frac{A_i}{\bar{A}_i}\gamma_i - \frac{A_j}{\bar{A}_j}\gamma_j\right]\frac{\bar{A}_j}{RT} \tag{3}$$

The above equations can then be solved after expressing the surface areas of the adsorbates and the surface activity coefficients as functions of the composition in the surface phase, which in turn are related to the bulk composition of the liquid mixture.

For a binary solution with components *i* and *j*, the surface mole fraction can be expressed as

$$x_i^{\sigma} = \frac{x_i^{l}}{x_i^{l} + \dfrac{\rho_j^{l}}{\rho_i^{l}}\dfrac{\rho_i^{*}}{\rho_j^{*}}x_j^{l}} \tag{4}$$

where

$$\frac{\rho_i^{*}}{\rho_j^{*}} = \frac{\rho_i^{\sigma}}{\rho_j^{\sigma}}\,\frac{\exp(\gamma_i - \gamma)A_i/RT}{\exp(\gamma_i - \gamma)A_j/RT} \tag{5}$$

$$= \frac{\rho_i^{\sigma}}{\rho_j^{\sigma}}\exp\frac{(\gamma_i A_i - \gamma_j A_j)}{RT}\exp\frac{(A_j - A_i)\gamma}{RT} \tag{6}$$

$$= (\rho_i^{\sigma}/\rho_j^{\sigma})(1/K_{\alpha}) \tag{7}$$

ρ here represents the activity coefficients, A is the cross-sectional area of the adsorbate, γ is the interfacial tension, R is the gas constant, T is the temperature, and K_{α} is a constant. This is the most general form of adsorption isotherm which depends on the following factors: (i) the activity coefficient ratio (ρ_i^{l}/ρ_j^{l}) in the bulk liquid phase, (ii) the activity coefficient ratio ($\rho_i^{\sigma}/\rho_j^{\sigma}$) in the surface phase, (iii) the magnitude of the term $\exp(\gamma_i A_i - \gamma_j A_j)/RT$, which may be considered to be the difference in the adsorption potentials of the two components, and (iv) the magnitude of the term $(A_j - A_i)\gamma/RT$, which may be considered to represent the variation of surface energy with the composition of the bulk solution.

Of these factors, the activity coefficient ratio (ρ_i^{l}/ρ_j^{l}) in the bulk liquid influences the nature of the isotherm profoundly. When the surface phase can be considered to be ideal and $A_i \cong A_j = A$, the term K_{α} equals $\exp(\gamma_j - \gamma_i)A/RT$ and is closely similar to the surface enrichment factor. Under these conditions, the free liquid surface and the adsorbed phase in contact with an inert solid can be compared directly (*1*). Using Young's equation

$$\gamma_{\mathrm{LS}} = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{LV}}\cos\theta \tag{8}$$

and the assumption that $\theta = 0$ for both liquids and for the solution, one can show that

$$(\gamma_{\mathrm{LV}})_j - (\gamma_{\mathrm{LV}})_i = (\gamma_{\mathrm{LS}})_i - (\gamma_{\mathrm{LS}})_j \tag{9}$$

It follows from the above discussion that if adsorption at these surfaces can be expressed in terms of unit surface, then the curves for the two surfaces must nearly be identical, except that one is turned 180° with respect to the other around the composition axis. This has been found to be free for a limited number of systems (*1*).

When the solutions behave in a nonideal manner, two different approaches have been suggested. The first is due to Schay and Nagy (*2*), who have shown that if m g of solid having a specific surface area S are equilibrated with n_0 mol of binary solution, then

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$$\frac{n_0\Delta x_i^{l}}{Sm} = \Gamma_i^{(N)} = -\frac{(1-x_i^{l})}{RT}\frac{d\gamma}{d\ln a_i^{l}} \tag{10}$$

where Δx_i^{l} is the change in the mole fraction of component due to adsorption. This equation is analogous to the Gibbs adsorption isotherm for the free liquid surface. From the above equation, it can be shown that

$$\gamma_i - \gamma = \frac{RT}{S}\int \frac{n_0\Delta x_i^{l}}{(1-x_i^{l})m}\, d\ln a_i^{l} \tag{11}$$

Further the surface composition x_i^{σ} can be written in terms of the amount of adsorption $(n_0\Delta x_i^{l}/m)$ thus

$$x_i^{\sigma} = \frac{Sx_i^{l} + A_j(n_0\Delta x_i^{l}/m)}{S + (A_j - A_i)(n_0\Delta x_i^{l}/m)} \tag{12}$$

It is, therefore, possible to calculate ρ_i^{σ} from

$$\ln \rho_i^{\sigma} = \ln a_i^{l} - \ln x_i^{\sigma} - (\gamma_i - \gamma)A_i/RT \tag{13}$$

the last two terms being from eq 11 and 12, respectively. To obtain $\gamma_i - \gamma$ a graphical integration method can be adopted in eq 11.

The second approach is that of Everett (*4*), where

$$n_0\Delta x_i^{l}/m = (n^{\sigma}/m)(x_i^{\sigma} - x_i^{l}) \tag{14}$$

and, if the ratio of activity coefficients $(\rho_i^{l}/\rho_j^{l})/(\rho_j^{\sigma}/\rho_i^{\sigma})$ in eq 4 and 5 can be approximated to unity, then

$$x_i^{\sigma} = \frac{x_i^{l}}{x_i^{l} + x_j^{l}/K_{\alpha}} = \frac{K_{\alpha}x_i^{l}}{K_{\alpha}x_i^{l} + x_j^{l}} \tag{15}$$

From eq 14 and 15, it follows that

$$\frac{n_0\Delta x_i^{l}}{x_j^{l}m} = n^{\sigma}\left(\frac{K_{\alpha}-1}{K_{\alpha}}\right) - \frac{n_0\Delta x_i^{l}}{m}\frac{1}{K_{\alpha}x_i^{l}} \tag{16}$$

where

$$K_{\alpha} = (a_i^{\sigma}/a_i^{l})(a_j^{l}/a_i^{\sigma})^{1/r}$$

From the above two equations, it follows that

$$\frac{x_i^{l}x_j^{l}}{n_0\Delta x_i^{l}/m} = \frac{m}{n^{\sigma}}\left[x_i^{l} + \frac{1}{1-K_{\alpha}}\right] \tag{17}$$

$$\ln \rho_j^{\sigma} = x_i^{\sigma}\ln\left[\frac{x_i^{\sigma}}{x_j^{\sigma}}\frac{a_j^{l}}{a_i^{l}}\right] - \int_0^{x_i^{l}} \ln\left(\frac{x_i^{\sigma}}{x_j^{\sigma}}\frac{a_j^{l}}{a_i^{l}}\right) dx_i^{\sigma} \tag{18}$$

The activity coefficients then can be calculated from the last equation. On replacing the x_i^{σ} and ρ_i^{σ} values of the two models in the equation given earlier (*7*), one can express the excess surface entropy values

$$S_E^{\sigma} = \sum_{i=1}^{r} \frac{Sx_i^{l} + a_j^{\sigma}(n_0\Delta x_i^{l}/m)}{S + (a_j^{\sigma} - a_i^{\sigma})(n_0\Delta x_i^{l}/m)}\left[\frac{\partial}{\partial T}RT\{\ln a_i^{l} - \ln a_i^{\sigma} - (\gamma_i - \gamma)a_i^{\sigma}/RT\}\right]_{x_i^{\sigma}} \tag{19}$$

$$S_E^{\sigma} = \sum_{i=1}^{r}\left[\left(\frac{n_0\Delta x_i^{l}}{m}\right)\frac{m}{n^{\sigma}} + x_i^{l}\right] \times \left[\frac{\partial}{\partial T}RTx_i^{\sigma}\ln\left(\frac{x_i^{\sigma}}{x_j^{\sigma}}\frac{a_j^{l}}{a_i^{l}}\right) - \int_0^{x_i^{\sigma}}\ln\left(\frac{x_i^{\sigma}}{x_j^{\sigma}}\frac{a_j^{l}}{a_i^{l}}\right)dx_i^{\sigma}\right] \tag{20}$$

Table I. Physical Properties of the Solvents Used[a]

property	temp, °C	solv: cyclohexane	solv: benzene	solv: dioxane
bp, °C		80.0 at 745 torr (80.08)	79.2 at 740 torr (79.25)	100.5 at 744 torr (100.63)
η,[b] g/cm^3	30	0.76926 (0.76928)	0.86843 (0.86845)	0.85504 (0.85500)
γ,[c] dyn/cm	20	24.96 (24.90)	28.90 (28.86)	33.70 (33.70)
	30	23.82 (23.81)	27.60 (27.58)	32.23 (32.20)
	40	22.59 (22.61)	26.36 (26.37)	30.86 (30.88)

[a] Values in parantheses indicate literature values. [b] Density. [c] Surface tension.

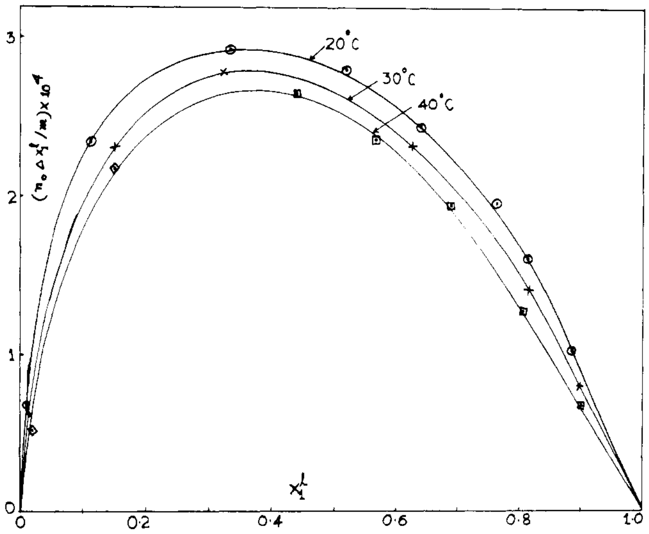

Figure 1. Composite adsorption isotherms of benzene–cyclohexane on alumina.

Experimental Section

The alumina used was of E-Merck grade and standarized for use in chromatography. The solid samples were washed 4–5 times with conductivity water, dried for 24 h at 150 °C, and powdered thoroughly each time before addition of solvents; the solids were dried overnight at 120 °C. The surface area of the solid was 65 m^2/g determined by the BET (N_2) adsorption method.

The solvents were purified according to standard procedure and their purities were checked from boiling point, surface tension, and density values (Table I). The details of the adsorption method have been described elsewhere (*6*) and will not be dealt with here. Since highly precise adsorption data were to be obtained, special care was taken to maintain the temperature accurate to ±0.2 °C in the thermostat where the ampules containing the solid and liquid were kept. Similar care was taken during measurement. The interferometer cell was kept at the same temperature and even the tubes used for transferring liquids from ampules to the cell.

Results and Discussion

The composite adsorption isotherms of benzene–cyclohexane and benzene–dioxane systems are presented in Figures 1 and 2, respectively. The *X* axis represents $n_0\Delta x_i^{l}/m$ and the *Y* axis indicates x_i^{l}. In all the cases $n_0\Delta x_i^{l}/m$ values decrease with rise in temperature. Such variation is normal, because with rise in temperature, the organic adsorbate will tend to leave the solid surface due to the rise in thermal kinetic energy. This effect becomes more pronounced in benzene–dioxane than in

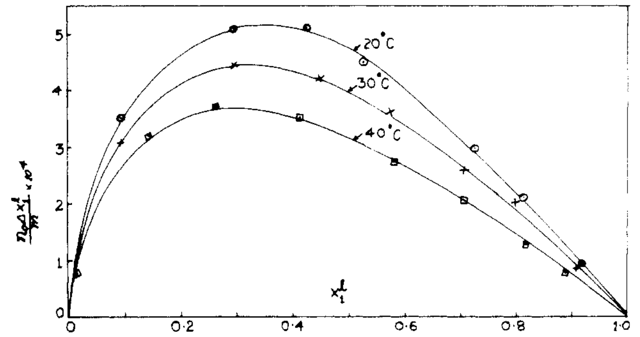

Figure 2. Composite adsorption isotherms of benzene–dioxane on alumina.

Table II. Amount of Adsorbate on Alumina Surface (mol/g × 10⁴)

soln	BET method	E and SN model		
		20 °C	30 °C	40 °C
benzene–cyclohexane	3.80	4.10	4.22	4.35 (E)
		5.80	5.53	5.30 (SN)
benzene–dioxane	3.96	4.70	5.11	5.32 (E)
		8.75	7.25	5.79 (SN)

benzene–cyclohexane. The difference in the $n_0 \Delta x_i^l/m$ values between any two temperatures is more than 5 times greater in benzene–dioxane than in benzene–cyclohexane. In fact, the effect of temperature on the adsorption of the latter system is insignificant. Similar remarkable changes were found in the cyclohexane–dioxane system (*8*). In both systems, component 1, i.e., benzene, is the preferentially adsorbed component.

The n^σ adsorbed values obtained from the two models are tabulated in Table II and compared with values obtained by using the BET (N_2) method. It can be observed that values derived from Everett's model are fairly comparable to the BET (N_2) value, especially in the benzene–cyclohexane system. The SN model gives values which are quite different from that of the BET (N_2) method. The order of deviation in the first set (Everett's model and the BET method) is ~10% while it is ~30% in the second set (SN model and BET values) for the benzene–cyclohexane system. However, both models (Everett and SN) show wide variation from the BET value in the benzene–dioxane system. Such variations are probably due to the fact that benzene–cyclohexane possesses more ideal characteristics than the benzene–dioxane mixture. The benzene–dioxane system tends to show even multilayer formation, indicating thereby greater specificity of interaction between dioxane and the surface sites on alumina, the interaction forces extending to multilayers.

The surface activity coefficients calculated according to the Everett and SN models are shown in Figures 3 and 4, respectively, for the benzene–cyclohexane and benzene–dioxane systems. In order to avoid too much data, values at only one temperature are plotted. It will be observed that while the surface mole fractions (x_i^σ) calculated by the two methods differ considerably for the same bulk composition, the plots of the log ρ_i^σ vs. x_i^σ in the figures agree reasonably well. Those based on the SN approach are somewhat larger than the corresponding Everett values. Here also it was observed that temperature in this range has but little effect on the nature of the surface layer in the case of benzene–cyclohexane. In the case of adsorption from the benzene–dioxane system, similar agreement is observed. When benzene–cyclohexane solutions are employed, the activity coefficient of benzene in the surface phase remains more or less constant over a wide composition range (x^σ(benzene) = 0–0.8) while that of cyclohexane does not, except at 40 °C. On the other hand, in the case of benzene–dioxane, it is the surface activity coefficient of dioxane which remains constant over a wide composition while that for benzene changes rapidly as composition is changed. Thus, the preferential nature of adsorbate is clearly brought out by the estimation of ρ_i^σ as a function of surface composition.

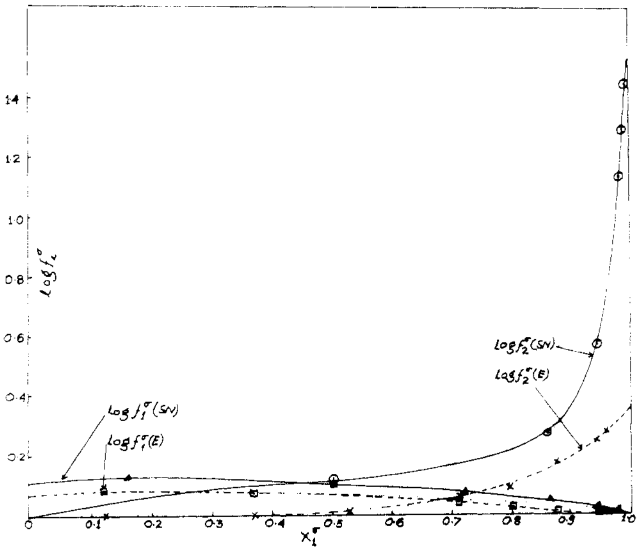

Figure 3. Surface activity coefficient for benzene–cyclohexane on alumina.

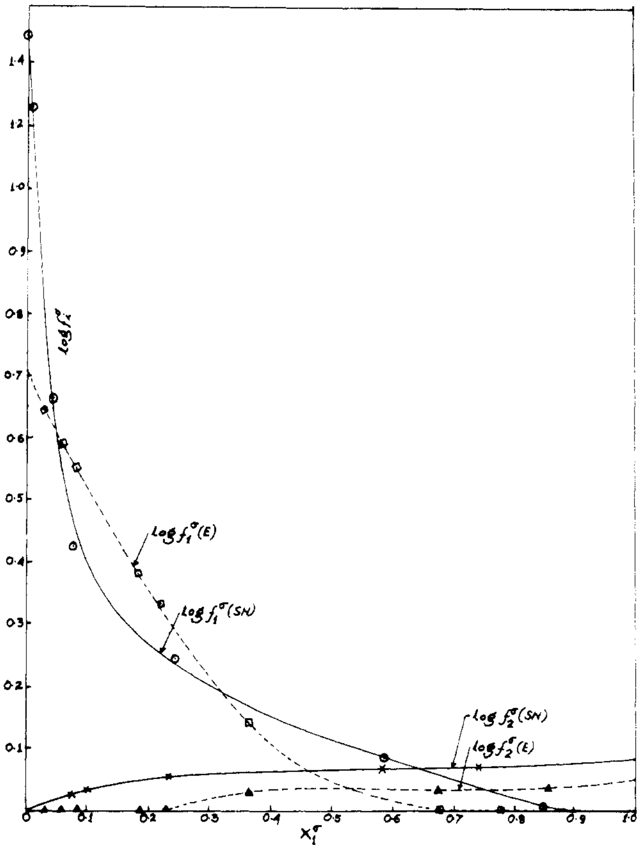

Figure 4. Surface activity coefficient for benzene–dioxane on alumina.

The excess surface entropy has been computed from the following equation:

$$S_E^\sigma = -\sum_{i=1}^{r} x_i^\sigma \left[\frac{\partial}{\partial_T}(RT \ln \rho_i^\sigma) x_i^\sigma \right] \qquad (21)$$

A plot of $RT \log \rho_i^\sigma$ vs. T on the basis of both models yielded a cluster of points fairly closely distributed about a single curve as the temperature was changed from 20 to 40 °C. Thus, the log ρ_i^σ could be considered to be independent of temperature in this temperature range. The excess surface entropy,

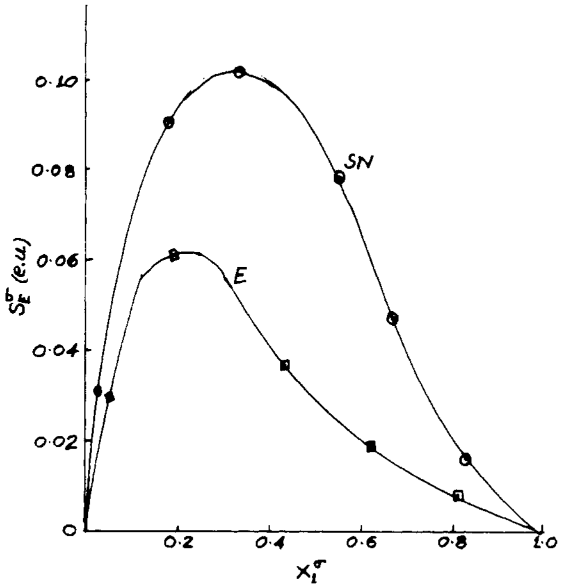

Figure 5. Excess surface entropy (S_E^σ) vs. surface mole fraction (x^σ) of benzene–dioxane on alumina.

therefore, reduces simply to $-R\sum x_i^\sigma \ln \rho_i^\sigma$ and, when plotted as a function of composition (x_i^σ), should yield a simple curve with one maximum. The curves obtained according to the S_E^σ values of two models are shown in Figure 5. Although the actual values from the two models are different, the natures of the curves are similar.

Conclusion

The adsorption of both benzene–cyclohexane and benzene–dioxane solutions decreases with a rise in the temperature range from 20 to 40 °C. This effect is more pronounced (~5 times) in benzene–dioxane than in benzene–cyclohexane. Benzene–cyclohexane solutions show multilayer adsorption. The surface activity coefficients are independent of temperature in this temperature range.

Glossary

σ	surface phase
l	bulk liquid
i	component 1
j	component 2
n_0	total amount of liquid mixture
Δx_i^l	change in mole fraction due to adsorption
m	mass of the solid
a	thermodynamic activity
S	specific surface area of solid
A	surface area of adsorbate
S_E^σ	excess surface entropy
T	temperature
R	gas constant
E	Everett's model
SN	Schay and Nagy's model
ρ^σ	surface activity coefficient
x^σ	surface mole fraction
γ	surface tension

Registry No. Alumina, 1344-28-1; benzene, 71-43-2; cyclohexane, 110-82-7; dioxane, 123-91-1.

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Measurement of the Volumetric Properties of Sulfur Hexafluoride from 260 to 340 K at Pressures to 2.5 MPa

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The volumetric properties of sulfur hexafluoride are determined experimentally by a Burnett apparatus at 260, 285, 315, and 340 K at pressures to 2.5 MPa. Compression factors are calculated by fitting simultaneously the isothermal pressure series to the Burnett relation and the virial equation. The calculated second virial coefficients agree well with available data from the literature. Densities and compression factors at integral pressures are calculated from the experimental data. The purity of the gas is 99.7%.

Burnett Apparatus

The gas-phase *PVT* properties are obtained by the Burnett method (*1*) in which only temperature and pressure measurements are required. The apparatus is identical with the one described by Fredenslund et al. (*2*) and Mollerup and Angelo (*3*). The Burnett cell consists of two thick-walled vessels of unspecified volume, here approximately 125 and 275 cm^3, connected to each other by means of an expansion valve. The Burnett cell is located in a thermostat and the larger volume connected to the pressure measuring system by means of a diaphragm differential pressure indicator. The pressure is measured on either an oil dead-weight piston gauge or an air dead-weight piston gauge depending upon the pressure range.

The larger vessel in the Burnett apparatus is evacuated and filled with the gas or gas mixture to be studied, and the smaller vessel is evacuated and kept under high vacuum. After isothermal conditions are obtained, the temperature and pressure are measured. The valve on the vent line to the vacuum system is closed and the expansion valve is then opened, and the pressure is allowed to equalize between the two vessels. The temperature and pressure are measured again after isothermal

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