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[Contribution from the School of Chemistry and Physics of the Pennsylvania State College]

The Heat of Adsorption of Nitrogen on Titanium Dioxide (Rutile) at 77.3°K.

By G. L. Kington and J. G. Aston

Terms in the expression for the isothermal heat of adsorption as given by Hill are shown to be the quantity known to previous authors as the heat of compression. The relationship between the *adiabatic* differential heat of adsorption and the heat of compression is deduced and the isothermal and adiabatic heats of compression related. The relationship between the calorimetric heat and isosteric heat is obtained and is shown to be independent of any assumption of a two-dimensional surface pressure. Differential heat of adsorption data for the system nitrogen on titanium dioxide (rutile) at 77.32°K., have been obtained in a precision adiabatic calorimeter and the data are described. Heat data have been obtained for the same system using the Clausius-Clapeyron relationship. These directly measured experimental values of the isosteric and calorimetric heats of adsorption have been compared and the validity of the theoretical relationship between these two quantities has been verified by the experimental data given. The value of the calorimetric heat of adsorption corrected for the adiabatic heat of compression is shown to agree within ±15 cal./mole (*i.e.*, ±0.9%) with the isosteric heat. There is no basis for considering calorimetric heats as usually measured, as obscure.

The field of adsorption has been obscured for some time due to statements[1,2] that the meaning of calorimetric heats as usually measured is uncertain. It is one of the aims of this paper to investigate the basis of such comments.

Differential heats of adsorption may be determined by three methods. A calorimetric measurement may be made under adiabatic or isothermal conditions, or the heat may be determined using the Clapeyron equation, *i.e.*, by the so-called isosteric method. It is of some importance to understand the significance of the quantities obtained from these three methods and to be able to relate them. Joyner and Emmett[3] have made a comparison of calorimetric and isosteric heats but the comparison is limited by the probable error in the calorimetric values which were determined by Beebe and estimated by him to have an accuracy of ±5%. Nevertheless, these calorimetric values are, in general, higher than the isosteric values. This may be explained by the fact that a correction for the heat of compression (as explained in the present paper) should be applied to the calorimetric values. Furthermore, if these heat quantities are to be of maximum value in helping to determine the state of the adsorbed phase, then calorimetric data must be determined with the highest possible accuracy.

It has been known for a considerable time that the calorimetric differential heat of adsorption includes a heat of compression. This aspect was discussed by Ward.[4] The adiabatic calorimetric heat of adsorption contains a so-called adiabatic heat of compression and the isothermal calorimetric heat of adsorption contains a corresponding isothermal heat of compression. The adiabatic and isothermal heats of compression are naturally different. The only possible uncertainty in a calorimetric measurement of a heat of adsorption is in the extent to which the heat of compression is conveyed to the calorimeter. This paper will show that in the usual type of adiabatic calorimeter the whole of the heat of compression appears in the calorimeter, within the experimental error.

Hill has recently obtained the relationship between the *isothermal* differential heat of adsorption and the isosteric heat. However, in practice the isothermal type of calorimeter is seldom used, since it has the disadvantage of operating at a few fixed temperatures, depending on the choice of the bath material. It is more advantageous to make measurements in a precision type of *adiabatic* calorimeter where the temperature may be controlled at will by electrical means, allowing isotherms, heat capacities and heats of adsorption or change of phase to be measured at any desired temperature. Precision adiabatic calorimeters have been developed for the measurement of heat capacities and this paper describes the use of such a calorimeter for measuring heats of adsorption and the data obtained. In order to interpret the data it has been necessary to investigate the theoretical basis of a heat of adsorption measurement in an adiabatic calorimeter, *i.e.*, the significance of the adiabatic heat of adsorption and the so-called adiabatic heat of compression.

Experimental

The Calorimetric Heat of Adsorption.—The calorimetric differential heat of adsorption of nitrogen on titanium dioxide was measured in the adiabatic calorimeter described by Morrison and Szasz.[5] The titanium dioxide was in the rutile crystalline form and had a surface area, as determined by the B.E.T. method, of 10.4 sq. m./g.

The heat effect accompanying the change in quantity of gas on the surface of a solid may be measured either as an adsorption process or as a desorption process. It is possible to measure an adsorption heat at any coverage of the surface,[6] but the determination of desorption heats is limited to that part of the surface (*i.e.*, above approximately one layer in this case) where the equilibrium gas pressure permits sufficient quantities of gas to be desorbed to give a measurable temperature change.

The majority of runs were made using the adsorption process, and covered the range 0 to 1.5 v/v_m. A smaller number of runs were carried out in desorption in the region 1 to 1.5 v/v_m. The maximum possible error in the calorimet-

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[1] Brunauer. "The Absorption of Gases and Vapors—Physical Adsorption," Princeton University Press, Princeton, N. J., 1943, Chapter 8.

[2] Hill, *J. Chem. Phys.*, **17**, 520 (1949).

[3] Joyner and Emmett, This Journal, **70**, 2356 (1948).

[4] Ward, *Proc. Roy. Soc. (London)*, **133A**, 506 (1931).

[5] Morrison and Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

[6] All surface coverages are expressed in terms of v/v_m, where v_m is obtained in the usual manner from the treatment of Brunauer, Emmett and Teller.

ric heat arising from errors in the temperature, pressure and volume measurements was estimated as ±15 cal./mole (*i.e.*, ±0.75% in 2,000 cal./mole). However, there are other possible sources of error not included in this figure. An error may be introduced into the adsorption process due to incomplete cooling of the incoming gas; this effect is, of course, not present in the desorption case. The results will show that with the calorimeter used this effect of incomplete heat exchange was negligible. The desorption heats may be subject to an error due to the difficulty in reducing the temperature of the adiabatic shields during the desorption process. This effect will be discussed later.

A summary of the calorimetric data obtained is given in Table I. Column 6 gives the differential heat of adsorption at the coverage indicated in column 4, and at an average temperature indicated in column 5. A temperature of 77.320°K. (normal boiling point of liquid nitrogen) was aimed at, as the average temperature for an increment. This temperature was not realized exactly and it was necessary to correct the heats to this standard temperature by using a calorimetrically determined temperature coefficient. The values of the calorimetric differential heat of adsorption corrected to 77.320°K. are given in column 7 of Table I; the same heats are shown as a function of surface coverage in Fig. 1.

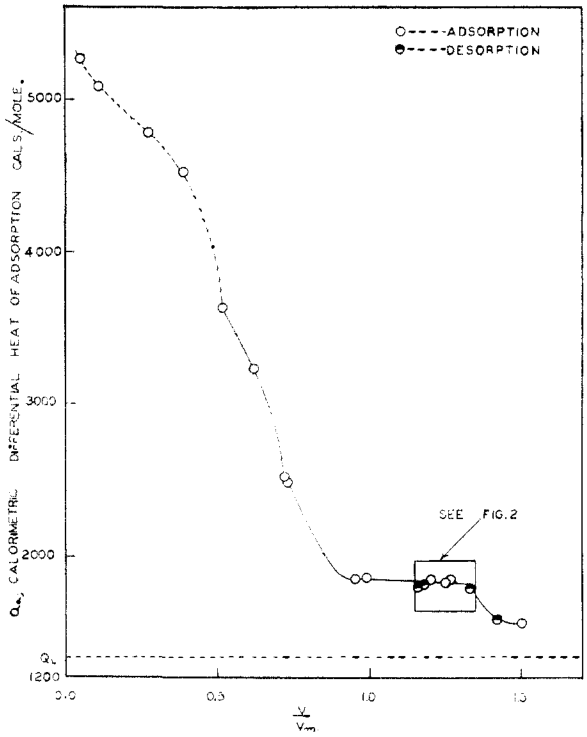

Fig. 1.—Calorimetric differential heat of adsorption, q_a, of nitrogen on titanium dioxide (rutile) at 77.3°K.

When an increment of gas was admitted to the calorimeter at a surface coverage less than $v/v_m = 0.5$, it was found that the time–temperature curve showed two regions. In the first 10 to 15 minutes a rapid temperature rise was noted; this was followed by a very slow increase in temperature which took place over a period of hours. These slow drifts were followed in some cases for about 4 hours. It should therefore be noted that the heats shown in column 6 of Table I, do not represent equilibrium values at coverages less than 0.5 v/v_m. The curve in Fig. 1 is shown as a broken line in this region. When the surface had been about half covered, the time–temperature relationship for an increment showed a marked change. The slow process disappeared and temperature equilibrium was attained in 20 to 25 minutes. Therefore, all points at coverages greater than 0.5 v/v_m represent equilibrium values. It should be emphasized that no slow temperature drift occurred when heat was introduced electrically during the course of a heat capacity measurement on the calorimeter plus clean adsorbent. In this determination the heat introduced was ten times the amount produced from an adsorption increment; furthermore, there was no gas pressure to facilitate heat conduction. Nevertheless, the calorimeter always attained temperature equilibrium in about 20 minutes. We therefore have definite evidence that when the first half of the surface is being covered the adsorption involves some slow process. This observation may help to elucidate the slow attainment of equilibrium noted when the heat capacity of the adsorbed film was being measured[5] in this apparatus. No further investigation was made of the slow process.

TABLE I

CALORIMETRIC DIFFERENTIAL HEAT OF ADSORPTION OF NITROGEN ON RUTILE AT 77.3°K.

(1) Run	(2) Method	(3) Note on rate	(4) v/v_m	(5) T, °K.	(6) q_a, cal./mole	(7) q_a (77.32 °K.) cal./mole
10	Adsorb	*a*	0.050	77.402	5261	
6	Adsorb	*a*	.108	77.396	5075	
11	Adsorb	*a*	.277	77.470	4780	
3	Adsorb	*a*	.390	77.808	4508	
21	Adsorb	..	.521	77.314	3632	3632
12	Adsorb	*b*	.622	77.461	3216	3207
22	Adsorb	*b*	.716	77.210	2500	2507
4	Adsorb	*b*	.727	77.388	2484	2479
13	Adsorb	*b*	.948	77.098	1828	1843
5	Adsorb	*b*	.988	77.038	1835	1854
17	Desorb	*b*	1.161	77.463	1795	1786
8	Desorb	*b*	1.176	77.384	1811	1807
9	Adsorb	*b*	1.201	77.423	1848	1841
14	Adsorb	*b*	1.250	77.233	1814	1820
24	Adsorb	*b*	1.265	77.363	1845	1842
25	Desorb	*b*	1.327	77.455	1789	1780
16	Desorb	*b*	1.423	77.652	1600	1578
15	Adsorb	*b*	1.497	76.942	1532	1557
Liquefaction[c]	....	..	...	77.32	..	1333

[a] Fast process followed by slow process. [b] Fast process only. [c] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

In general it should be noted from Fig. 1 that the differential heat of adsorption of the first increment of nitrogen admitted to the surface was about 5.2 kcal./mole. The heat values then show a rapid decrease and reach a value of about 1.8 kcal./mole at the monolayer. There is then a very marked plateau up to 1.3 v/v_m, where the differential heat of adsorption shows very little change. Beyond this coverage the heats again decrease and approach the heat of liquefaction of nitrogen, 1,333 cal./mole.

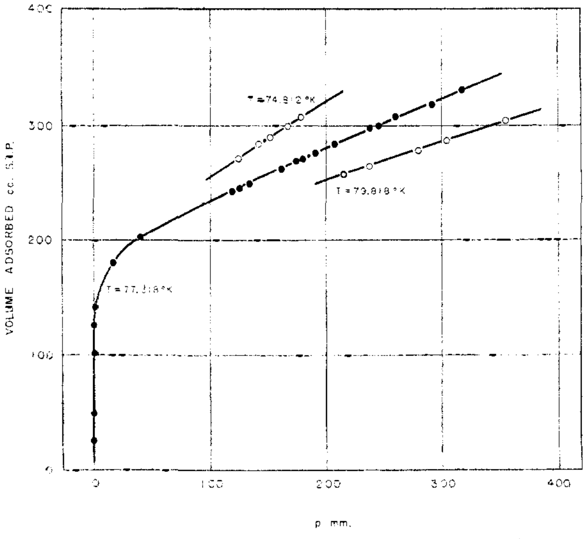

Fig. 2.—Isotherm of nitrogen on titanium dioxide (rutile).

Isosteric Heats.—In order to obtain accurate isosteric heat data, it was decided to make detailed isotherm observations in the region 1.15 to 1.35 v/v_m. Isotherms were measured in this region, at 74.812, 77.318 and 79.818°K. and are shown graphically in Fig. 2. Pressure measurements were made, using a cathetometer, with a maximum error of ±0.01 mm. on each arm. The maximum deviation of the temperature of any point from the isotherm temperature was ±0.006°K. The over-all maximum error in the isosteric heats was estimated as ±10 cal./mole (*i.e.*, ±0.5% in 2,000 cal./mole). The heats were calculated using the expression

$$q_{is} = R\left(\frac{T_1T_2}{T_2 - T_1}\right)(\ln p_2 - \ln p_1)\left\{1 - \frac{\alpha(p_1 + p_2)}{2}\right\}$$

where α is the fractional deviation per atmosphere of the volume from ideality. It was thus possible to make three sets of calculations of q_{is} from the three isotherms, this gave the isosteric heat as a function of coverage at 76.065, 78.568 and 77.315°K. These results are indicated in columns 2, 3, 4 of Table II. The average of the heats indicated in columns 2 and 3 is shown in column 5. The final values of the isosteric heats, corrected for the non-ideality of nitrogen gas under the experimental conditions, are given in column 6 of Table II, and are also shown in Fig. 3.

TABLE II

ISOSTERIC HEATS OF ADSORPTION OF NITROGEN ON RUTILE

(1) Adsorbed gas cc. S.T.P.	(2) 76.065°	(3) 78.568°	(4) q_{st}, cal./mole 77.315°	(5) 77.316°	(6) 77.320°
265.00	1711	1727	..	..	1701
275.00	1711	1726	1718	1718	1696
279.20	1704	1720	1712	1712	1690
285.00	1690	1738	1714	1714	1690
295.00	1691	1722	1706	1706	1679
305.00	1679	1702	1690	1690	1661

Discussion and Final Results

Hill has considered a process taking place in an isothermal calorimeter, closed by a movable piston, and he has deduced that the isothermal heat of adsorption[7] (converting to molal quantities) is given by

$$q_{th} = V_g(\partial p/\partial n_s)_T + RT + \bar{E}_g - \bar{E}_s - n_s(\partial \bar{E}_s/\partial n_s)_T \quad (1)$$

where V_g is the volume of the gas phase in the calorimeter, n is the total number of adsorbable moles in the calorimeter; of this total number of moles, n_s moles are in the adsorbed state and n_g are in the gas state; $\bar{E}_g$ is the molal energy of the gas phase and $\bar{E}_s$ is the average molal energy of the adsorbed gas. In order to relate this expression, Eq. (1), to concepts put forward by previous authors, it is necessary to invest the mathematical formalism with some physical significance. It is not immediately obvious that the first two members of the right hand side of Hill's expression, Eq. (1), constitute the quantity usually designated as the heat of compression.

It is instructive to deduce this differential heat of compression as follows. If the volume of the gas phase (here assumed perfect) be changed by δV_g, then the heat liberated is $-p\delta V_g$. The differential quantity per mole, which we will denote by q_c, is then given (as $\delta n_s \rightarrow 0$) by

$$q_c = -p(\delta V_g/\delta n_s) \quad (1a)$$

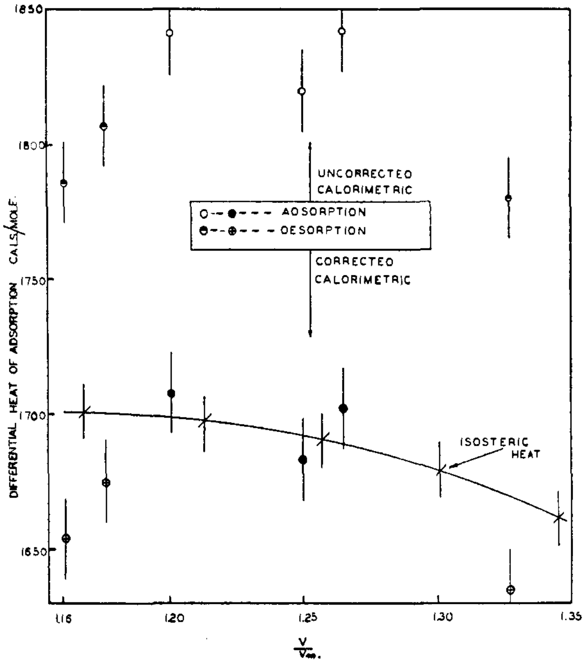

Fig. 3.—Calorimetric heats (corrected and uncorrected) and isosteric heats. The solid circles and crossed circles represent corrected values for adsorption and desorption, respectively.

assuming the perfect gas law

$$pV_g = n_gRT$$

$$p\delta V_g + V_g\delta p = -RT\delta n_s + n_gR\delta T$$

Substituting in Eq. (1a) gives

$$q_c = V_g(\delta p/\delta n_s) + RT - n_gR(\delta T/\delta n_s) \quad (2)$$

It should be noted that for any equilibrium involving a *pure* condensed phase at constant T, Eq. (2) requires the heat of compression to be RT. This is, of course, the usual external work involved in the evaporation of a mole of *pure* liquid. For any system involving a solution, all three terms of Eq. (2) must be considered. Equation (2) gives the differential heat of compression for the general case, *i.e.*, no requirement of an isothermal process has been introduced. The isothermal differential heat of compression q_{ci} is then obtained from Eq. (2) as

$$q_{ci} = -p(\partial V_g/\partial n_s)_T = V_g(\partial p/\partial n_s)_T + RT \quad (3)$$

It is thus apparent that the first two terms in Hill's relationship for q_{th} are in fact the differential isothermal heat of compression. Furthermore, it is seen that this heat of compression may be readily obtained from a knowledge of the slope of the isotherm. Hill's relationship, Eq. (1), therefore enables us to correct the calorimetrically measured differential *isothermal* heat of adsorption for the *isothermal* heat of compression.

The Adiabatic Adsorption Calorimeter.—Consider an adiabatic calorimeter closed by a movable piston. In the initial state the total energy of the calorimeter plus solid, gas phase and adsorbed gas is given by

$$E = E_c + (n - n_s)\bar{E}_g + n_s\bar{E}_s \quad (4)$$

If the piston be moved, changing the volume of the gas phase by δV_g, then

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[7] The following symbols will be used to denote the various heat quantities: q_{th}, isothermal differential heat of adsorption; q_{ci}. isothermal differential heat of compression; q_a, adiabatic differential heat of adsorption; q_{ca}, adiabatic differential heat of compression; q_{st}. isosteric heat. In all cases where Hill has symbolized these quantities, his symbols are maintained at the sacrifice of uniformity in our system.

$$\delta E + p\delta V_g = 0 \tag{5}$$

$$\delta E = \delta E_c + n_g\delta\bar{E}_g - \bar{E}_g\delta n_s + n_s\delta\bar{E}_s + \bar{E}_s\delta n_s \tag{6}$$

When the piston changes the volume of the gas phase by δV_g, δn moles are transferred between the gas phase and the adsorbed phase, and the temperature of the calorimeter and its contents changes by δT. The adiabatic calorimetric heat of adsorption is defined by

$$q_a = (C_c + n_g\bar{C}_g + n_s\bar{C}_s)(\delta T/\delta n_s)_S \tag{7}$$

where C_c is the heat capacity of the calorimeter and solid, and $\bar{C}_g$ and $\bar{C}_s$ are the molar heat capacities at constant pressure of the gas phase and adsorbed gas, respectively.

It is now necessary to obtain expressions for δE_c, $\delta\bar{E}_g$ and $\delta\bar{E}_s$ in Eq. (6). If we assume that the calorimeter and solid are unaffected by the adsorption process at constant temperature, then

$$\delta E_c = (\partial E_c/\partial T)_{n_s}\delta T = \bar{C}_c\delta T \tag{8}$$

also

$$\delta\bar{E}_g = \bar{C}_g\delta T \tag{9}$$

and

$$\begin{aligned}\delta\bar{E}_s &= (\partial\bar{E}_s/\partial T)_{n_s}\delta T + (\partial\bar{E}_s/\partial n_s)_T\delta n_s\\ &= \bar{C}_s\delta T + (\partial\bar{E}_s/\partial n_s)_T\delta n_s\end{aligned} \tag{10}$$

Combining Eqs. (8), (9) and (10) with Eqs. (5) and (6)

$$C_c\delta T + n_g\bar{C}_g\delta T - \bar{E}_g\delta n_s + n_s\bar{C}_s\delta T + n_s(\partial\bar{E}_s/\partial n_s)_T\delta n_s + \bar{E}_s\delta n_s + p\delta V_g = 0$$

Rearranging and substituting from Eq. (7)

$$q_a = -p(\partial V_g/\partial n_s)_S + \bar{E}_g - \bar{E}_s - n_s(\partial\bar{E}_s/\partial n_s)_T \tag{11}$$

It is now necessary to evaluate the adiabatic differential heat of compression $q_{ca} = -p(\partial V_g/\partial n_s)_S$, and to compare it with the isothermal differential heat of compression $q_{ci} = -p(\partial V_g/\partial n_s)_T$. It has been shown that in general the differential heat of compression is given by Eq. (2). Thus, the adiabatic differential heat of compression is given by

$$q_{ca} = V_g(\partial p/\partial n_s)_S + RT - n_gR(\partial T/\partial n_s)_S \tag{12}$$

where the partial derivative is at constant entropy. But

$$p = f(T, n_s)$$

Therefore

$$\delta p = (\partial p/\partial T)_{n_s}\delta T + (\partial p/\partial n_s)_T\delta n_s$$

$$(\partial p/\partial n_s)_S = (\partial p/\partial T)_{n_s}(\partial T/\partial n_s)_S + (\partial p/\partial n_s)_T \tag{13}$$

Substituting Eq. (13) in Eq. (12)

$$q_{ca} = V_g(\partial p/\partial n_s)_T + RT + [V_g(\partial p/\partial T)_{n_s} - n_gR](\partial T/\partial n_s)_S \tag{14}$$

Eq. (14) is a valuable relationship enabling us to deduce the adiabatic heat of compression from the experimental data. Comparing Eq. (14) with Eq. (13), it is seen that the adiabatic and isothermal differential heats of compression are related by

$$q_{ca} = q_{ci} + [V_g(\partial p/\partial T)_{n_s} - n_gR](\partial T/\partial n_s)_S \tag{15}$$

The complete relationship for the *adiabatic* differential heat of adsorption is obtained by combining Eq. (14) and Eq. (11).

$$q_a = V_g(\partial p/\partial n_s)_T + RT + [V_g(\partial p/\partial T)_{n_s} - n_gR](\partial T/\partial n_s)_S + \bar{E}_g - \bar{E}_s - n_s(\partial\bar{E}_s/\partial n_s)_T \tag{16}$$

where the first three members of the right-hand side of the expression represent the *adiabatic* heat of compression. It should be noted that the *isothermal* differential heat of adsorption has been given by Hill as

$$q_{th} = V_g(\partial p/\partial n_s)_T + RT + \bar{E}_g - \bar{E}_s - n_s(\partial\bar{E}_s/\partial n_s)_T \tag{17}$$

where the first two members of the right-hand side represent the *isothermal* heat of compression.

The Isosteric Heat of Adsorption.—In a strictly thermodynamic treatment of an adsorption system, as distinct from the statistical mechanical approach, it is unnecessary to postulate a specific model for the adsorbed phase. In particular in discussing the thermodynamics of heats of adsorption it is not necessary to introduce a concept of a surface pressure as is done by Hill.[2] The surface pressure of a gas adsorbed on a solid is not a directly measurable quantity and as such need not be considered explicitly in thermodynamic equations.[8] While the usefulness of the treatment of two-dimensional surface pressure along the lines of Harkins and Jura is not disputed, it does, however, produce needless terms when discussing the thermodynamics of heats of adsorption. Nevertheless, it is recognized that the implications of a surface pressure must be considered in any statistical treatment of the adsorbed phase. We will show that any relationship between calorimetric and isosteric heats is completely independent of any model of the adsorbed phase and in particular no concept of surface pressure is involved. Consider the total Gibbs free energy G[9] of a calorimeter plus solid and adsorbed gas (but excluding the gas phase); then

$$(\partial G/\partial T)_{p,n_s} = -S \tag{18}$$

where S is the total entropy of the calorimeter plus solid and adsorbed gas, and

$$(\partial G/\partial p)_{T,n_s} = V \tag{19}$$

where V is the total volume of the calorimeter plus solid and adsorbed gas. We will now differentiate the expressions (18) and (19) with respect to n_s, the total number of moles adsorbed.

$$\partial(\partial G/\partial T)/\partial n_s = -(\partial S/\partial n_s)$$

or defining μ by

$$\mu = (\partial G/\partial n_s)_{T.p}$$

$$(\partial\mu_s/\partial T)_{p.n_s} = -\bar{S}_s \tag{20}$$

$\bar{S}_s$ is then the partial molal entropy of the adsorbed gas; similarly

$$(\partial\mu_s/\partial p)_{T.n_s} = \bar{V}_s \tag{21}$$

where $\bar{V}_s$ is the partial molal volume of the adsorbed gas. The partial molal free energy of the adsorbed gas is dependent on the variables T,p,n_s. Then

$$\delta\mu_s = (\partial\mu_s/\partial T)_{p,n_s}\delta T + (\partial\mu_s/\partial p)_{T.n_s}\delta p + (\partial\mu_s/\partial n_s)_{P.T}\delta n_s$$

and for the gas phase

$$\delta\mu_g = (\partial\mu_g/\partial T)_p\delta T + (\partial\mu_g/\partial p)_T\delta p$$

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(8) While we had recognized this as a consequence of the principle that thermodynamics cannot distinguish a specific mechanism nor take cognizance of internal variables, our ideas were clarified by a discussion with C. J. Gorter (Leiden) about his paper (which is in course of publication).

(9) To maintain uniformity with recent literature, G is used for the Gibbs free energy and μ for the partial molal free energy of Lewis (thermodynamic potential).

Stating the condition for equilibrium

$$\delta\mu_s = \delta\mu_g$$

and substituting for the free energy coefficients from Eqs. (20) and (21)

$$-S_s\delta T + \bar{V}_s\delta p + (\partial\mu_s/\delta n_s)_{p,T}\delta n_s = -\tilde{S}_g\delta T + \tilde{V}_g\delta p$$

Dividing by δT and passing to the limit at constant n_s

$$(\partial p/\partial T)_{n_s} = (\tilde{H}_g - \bar{\bar{H}}_s)/[(\tilde{V}_g - \bar{V}_s)T] = q_{st}/[(\tilde{V}_g - \bar{V}_s)T](i.e.,\ q_{st} = \tilde{H}_g - \bar{\bar{H}}_s) \quad (22)$$

Thus any term in φ (the two dimensional surface pressure) is contained in $\bar{\bar{H}}_s$, whereas Hill's expression for q_{st} explicitly contains a term involving φ. By definition

$$\tilde{H}_g = \tilde{E}_g + p\tilde{V}_g$$

and

$$\bar{\bar{H}}_s = \bar{E}_s + p\bar{V}_s$$

Substituting in Eq. (22) for $\tilde{H}_g$ and $\bar{\bar{H}}_s$

$$q_{st} = \tilde{E}_g + p\tilde{V}_g - \bar{E}_s - p\bar{V}_s \quad (23)$$

But

$$\bar{E}_s = [\partial(E_c + n_s\tilde{E}_s)/\partial n_s]_T$$

We will make the assumption that the thermodynamic properties of the calorimeter and solid are unchanged by the adsorption process at constant temperature. Then

$$\bar{E}_s = n_s(\partial\tilde{E}_s/\partial n_s)_T + \tilde{E}_s \quad (24)$$

Substituting Eq. (24) in Eq. (23)

$$q_{st} = \tilde{E}_g - \tilde{E}_s - n_s(\partial E_s/\partial n_s)_T + p(\bar{V}_g - \tilde{V}_s) \quad (25)$$

We will now make the assumption that the volume of the adsorbed phase is negligible, ($\tilde{V}_s = 0$), and assume that the gas phase obeys the perfect gas law. Then Eq. (25) becomes

$$q_{st} = \tilde{E}_g - \tilde{E}_s - n_s(\partial\tilde{E}_s/\partial n_s)_T + RT \quad (26)$$

It is now possible to relate the isosteric heat with the adiabatic heat of adsorption. Comparing Eq. (26) and (16) it is seen that

$$q_a = q_{st} + V_g(\partial p/\partial n_s)_T + [V_g(\partial p/\partial T)\,n_s - n_g R](\partial T/\partial n_s)_S \quad (27)$$

Furthermore, considering the relationship for the adiabatic heat of compression in Eq. (14), it is evident that

$$q_{st} = q_a - (q_{ca} - RT)$$

Also, it is of interest that

$$(\tilde{H}_g - \bar{\bar{H}}_s) = (q_a - q_{ca}) + RT \quad (28)$$

Comparison of Calorimetric and Isosteric Heats.—Column 2 of Table III shows the calorimetrically determined values of the adiabatic differential heat of adsorption. Column 3 gives the experimental isosteric values at the same surface coverage. It is seen that in all cases a calorimetric heat is greater than the isosteric heat by about 100 cal./mole. The actual differences are given in column 4 of Table III. The theoretical treatment at the beginning of this paper shows that the adiabatic heat, the isosteric heat and the heat of compression are related by Eq. (27) and (14). It was shown that the adiabatic heat of adsorption is greater than the isosteric heat by a quantity which is less than the heat of compression by *RT*. We have therefore calculated $(q_{ca} - RT)$ from Eq. (14) for each coverage and have tabulated the results in column 5 of Table III. Comparing these figures with the experimental differences found in column 4, it is seen that the agreement is good. It should be noted that the figures in column 4 are subject to an estimated maximum error of ±25 cal./mole.

TABLE III

CALORIMETRIC HEATS, ISOSTERIC HEATS AND HEATS OF COMPRESSION FOR THE ADSORPTION SYSTEM NITROGEN–TITANIUM DIOXIDE AT 77.32°K.

Column (2) q_a, estimated maximum error ± 15 cal./mole.
Column (3) q_{st}, estimated maximum error ± 15 cal./mole.

(1)	(2) Calorimetric heat q_a, cal./mole			(3) Isosteric heat, q_{st} cal./mole	(4) Cal./mole	(5) $(q_{ca} - RT)$, cal./mole	(6) q_a corrected, cal./mole
v/v_m	Run	Method	q_a				
1.161	17	*d*	1786	1702	84	132	1654
1.176	8	*d*	1807	1700	107	132	1675
1.201	9	*a*	1841	1698	143	133	1708
1.250	14	*a*	1820	1692	128	137	1683
1.265	24	*a*	1842	1688	154	140	1702
1.327	25	*d*	1780	1669	111	145	1635

[a] Indicates measurement was made in adsorption. [d] Indicates measurement was made in desorption.

These results may be expressed in a somewhat different manner as follows. The theoretical treatment shows that the experimental calorimetric value q_a should have the quantity $(q_{ca} - RT)$ subtracted from it to give the calorimetric heat of adsorption corrected for the heat of compression. This corrected calorimetric heat should be identical with the isosteric heat. In Fig. 3 a plot has been made of the experimental isosteric heats and a curve has been drawn through these points. The experimental calorimetric heats are plotted in the same figure as open circles and half-open circles. The length of the vertical line on all points in this figure indicates the estimated error for that point. The corrected calorimetric heats are shown as black circles and crossed circles (the actual figures are given in column 6 of Table III). It is seen that the corrected calorimetric heats measured in adsorption agree within ±15 cal./mole (*i.e.*, ±0.88%) with the isosteric heat curve. The corrected calorimetric heats measured in desorption differ from the isosteric heat curve by a quantity which is somewhat greater than the estimated maximum error. It is possible that this error in the desorption experiments arises because of the difficulty in maintaining adiabatic conditions around the calorimeter when the temperature of the system is decreasing.

From the evidence presented in Table III and Fig. 3 it is apparent that the corrected calorimetric heats and isosteric heats are identical within ±15 cal./mole, *i.e.*, ±0.9%. It must be emphasized that this is only true if the calorimetric heats are fully corrected for the compression effect, and corrections have been made for the non-perfect nature of the adsorbate gas when calculating isosteric heats. Furthermore, we must conclude that the whole of the heat of compression appears in the calorimeter and that there is no further basis for considering calorimetric values of the heat of adsorption as usually measured, as obscure.

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A Correlation of the Thermodynamic Properties of Nitrogen Absorbed on Titanium Dioxide[1]

BY G. L. KINGTON AND J. G. ASTON

A comparison of the experimental thermodynamic properties with those calculated from the B.E.T. theory indicates that this or any other theory with such simplified assumptions will be inadequate to predict a set of thermodynamic properties which are even qualitatively consistent.

This paper is concerned with the adsorbed phase of nitrogen on titanium dioxide (rutile). Previous publications from this Laboratory have reported data for the identical system. The heat capacity of a monolayer was given by Morrison and Szasz.[2] The differential heat of adsorption was discussed by Kington and Aston.[3] We now present some thermodynamic functions derived from experimental data and the corresponding quantities required by the B.E.T. theory.

Method of Comparison and Results

Differential and Partial Molal Quantities.—The method of calculating the partial molal entropy of a film and the requirements of the B.E.T. theory for this quantity have been adequately discussed previously[4] for other systems, but hitherto the experimental data have not been sufficiently accurate to make anything but general conclusions. The partial molal entropy of the present system of nitrogen on rutile is shown in Fig. 1; curve 1 refers to the values obtained from the experimental data. These values were obtained by subtracting the quantity $\bar{H}_g - \bar{H}_s$ from the value of $\bar{F}_g - \bar{F}_s$. The former values were obtained from the measured differential heats, q_d, reported previously[3] by applying equation 28 of that paper[3] connecting the two quantities. They are graphed in Fig. 3. The values of $\bar{F}_g - \bar{F}_s$ were obtained from our own data on the isotherms plotted as $\bar{F}_1 - \bar{F}_s$ in Fig. 2. In view of the fact that no two samples of rutile are alike, tabulated values of these data are of no particular use. It is seen that the curve for the partial molal entropy as a function of θ, obtained from the experimental data is in general agreement for the system reported previously,[4] *i.e.*, the partial molal entropy of the film is much lower than the entropy of the bulk liquid or solid phases at coverages less than a monolayer, the partial molal entropy of the film becoming approximately equal to the molal entropy for a liquid at coverages greater than a monolayer.

The thermodynamic functions required by the B.E.T. theory are dependent on the value of c and of j_s/j_1, since

$$c = (j_s/j_1)e^{(\epsilon_1 - \epsilon_1)/RT}$$

The value of c may be fixed from a knowledge of the experimental isotherm data, then the functions q, $\bar{S}_s$ and S_s required by the B.E.T. theory may be calculated if a value can be assigned to j_s/j_1.

In the absence of any information on this ratio, the original postulate of the B.E.T. theory was that $j_s = j_1$. However, there has been considerable discussion on the value to be given to j_s/j_1. Cassie[5] has suggested $j_s/j_1 = 1/50$, Hill[6] has disagreed with this point of view and indicates that $j_s/j_1 > 1$.

The value of c for our system has been determined as 120 from the isotherm data in the usual manner. Expressed in a somewhat different manner this means that the differential free energy required by the B.E.T. theory is in agreement with the free energy required by the experimental data (over a certain range of x) if c be chosen to be 120. A plot of the differential free energy from experimental data and using $c = 120$ in the B.E.T. theory is shown in Fig. 2. It is seen that there is good agreement above $\theta = 0.7$, but that below this surface coverage the B.E.T. theory departs from experiment rather markedly.

Having determined, for a certain range of θ, that the B.E.T. free energy requires $c = 120$, we will now use this value of c to calculate the partial molal entropy of a film required by B.E.T. theory. We can now take various values of j_s/j_1 and investigate the behavior of the partial molal entropy of the B.E.T. film as a function of coverage. Values of j_s/j_1 of 1, 75 $\times 10^{-3}$ and 6.3 $\times 10^{-3}$ have been taken and the respective values of $\bar{S}_s$ are shown in curves 2, 3 and 4 of Fig. 1. It is seen that taking a small value of j_s/j_1 gives a much more realistic curve for $\bar{S}_s$, since the experimental curve (1), requires the value of this function to be less than the molal entropy of the liquid phase at coverages less than $\theta = 1$.

A further result of taking a small value for j_s/j_1 is seen in its effect on the differential heat of adsorption required by the B.E.T. theory. Since the B.E.T. theory gives a fair indication of the free energy change in an adsorption process (see Fig. 2) then the wide divergence between the partial molal entropy required by the B.E.T. theory (assuming

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