(ii) **Carbonyl Overtone.**—Since carbonyl groups produce strong absorption bands in the region 1780–1620 cm.$^{-1}$, weak overtone bands may be expected at approximately twice this frequency range, *viz.*, 3560–3240 cm.$^{-1}$. Such bands overlap the regions of the OH and NH stretching bands and may confuse the interpretation of weak bands in this region, though no cases of this have yet been encountered.

(iii) **Bands between 1640 and 1550 Cm.$^{-1}$.**—Bands of moderate intensity are frequently observed in the region 1640–1550 cm.$^{-1}$ (see Table III). Such bands generally indicate unsaturation in the molecule (C=C, C=N stretching vibrations), though there is the possibility that they could be caused by NH bending vibrations.[5] Phenyl rings generally give absorption bands in the ranges 1640–1615 or 1605–1600 cm.$^{-1}$ while alkaloids containing aromatic nitrogen rings (*e. g.* pyridine, quinoline rings) generally give bands between 1600 and 1560 cm.$^{-1}$. Thus the bands at 1592 and 1576 cm.$^{-1}$ present in the spectrum of anabasine but absent from the spectrum of piperidine (see Fig. 1) may be assigned to the pyridine ring. Similarly the band between 1570 and 1566 cm.$^{-1}$ found in the spectra of cytisine, N-methylcytisine, thermopsine and anagyrine may be assigned to the α-pyridone ring (II). The observation of bands in this region gives an indication of the types of structure which might be present but does not permit an unambiguous choice to be made owing to the multiple interpretations possible (*viz.*, cevine and jervine).

(iv) **Bands at Lower Frequencies.**—The spectra included in this survey do not extend beyond 1540 cm.$^{-1}$ due to the strong absorptions of the chloroform. Satisfactory spectra are obtained, however, by using Nujol mulls[2a] or thin films of the alkaloids. A great deal of complex structure is found in the region 1500–600 cm.$^{-1}$, and as yet the assignment of bands in this region to specific groups in the molecule is comparatively undeveloped. The chief value of such spectra lies in this high specificity, which offers a very delicate method for the identification of individual alkaloids. Thus they have been used to confirm the identity of monolupine, rhombinine and anagyrine.[11]

Acknowledgments.—The authors wish to thank Mr. R. Lauzon for technical assistance in the measurement of the spectra.

Summary

1. The infrared absorption spectra of forty-seven alkaloids have been investigated in the region 3700–1540 cm.$^{-1}$ in dilute chloroform solution.

2. Hydroxyl groups may generally be detected by the appearance of a sharp band in the region 3625–3540 cm.$^{-1}$ with an apparent molecular extinction coefficient of 30–160 though there are exceptions.

3. Imino groups produce a sharp band in the region 3480–3440 cm.$^{-1}$ with an apparent molecular extinction coefficient of 100–210 when the imino group is present in an indole nucleus or secondary amido group. When the imino group is present in a piperidine ring, however, the absorption is much weaker but may be observed at increased path lengths.

4. Carbonyl groups may be detected by the appearance of a strong band in the region 1780–1620 cm.$^{-1}$ with an apparent molecular extinction coefficient from 300–1200. Certain correlations have been established between the carbonyl frequency and the type of carbonyl group present.

5. Phenyl rings generally give absorption bands in the region 1640–1600 cm.$^{-1}$ while aromatic nitrogen rings generally give bands between 1600 and 1560 cm.$^{-1}$.

6. The presence of a carbonyl group both in cevine and jervine is indicated by the infrared absorption spectra.

[11] Marion and Ouellet, THIS JOURNAL, **70**, 3076 (1948).

OTTAWA, CANADA RECEIVED MAY 27, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Energetics of the Adsorption of Aliphatic Amines by Silica Gel[1]

BY DONALD G. DOBAY,[2] YING FU AND F. E. BARTELL

In a previous communication[3] adsorption isotherms of diethylamine, *n*-butylamine and di-*n*-butylamine on silica gel at 25° were presented and their significance as relating to the nature of the adsorption process discussed. In the present paper these adsorption systems will be considered from the basis of energy changes.

Isosteric Heats, $\overline{\Delta H}$, $\overline{\Delta F}$ and $\overline{\Delta S}$ of Adsorption.—In order to determine the isosteric heats, adsorption isotherms for these amines at 40° were obtained and the pressure range employed was from zero to a value higher than that corresponding to the inception of the hysteresis effect. These data are given in the first column of Table I. The isosteric heats were calculated by means of the Clapeyron equation

$$dQ/d(x/m) = RT_1T_2\log_e (p_1/p_2)/(T_1 - T_2) \qquad (1)$$

where $dQ/d(x/m)$ represents the differential isosteric heats of adsorption and the p-values represent the pressures at which equal amounts of the amines were adsorbed by the solid at the two different temperatures. This method of calculating the isosteric heats requires that the surface area of the solid be considered as being independent of the temperature. While this is not strictly true, the

---

[1] A portion of the material in this paper is from a dissertation submitted to the Horace H. Rackham School of Graduate Studies by Donald G. Dobay in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1948.

[2] Linde Air Products Company, Tonawanda, N. Y.

[3] Bartell and Dobay, THIS JOURNAL, **72**, 4388 (1950).

TABLE I

DIFFERENTIAL ISOSTERIC HEATS, $\overline{\Delta H}$, $\overline{\Delta F}$ AND $\overline{\Delta S}$ OF ADSORPTION OF AMINE VAPORS BY SILICA GEL, (ALL IN KILOCALORIES/MOLE)

x/m mg./g.	P_1/P_{1_0} (40°)	P_2/P_{2_0} (25°)	$\frac{dQ}{d(x/m)}$	$-\overline{\Delta H}$	$-\overline{\Delta F}_{25°}$	$-\overline{\Delta F}_{40°}$	$-\overline{\Delta S}$,[a]	$-\overline{\Delta S}$,[b]
				Diethylamine				
81.7	0.020	0.00175	38.1	30.4	3.76	2.43	89.3	88.7
86.4	.048	.0044	37.2	29.5	3.21	1.89	87.1	87.0
95.5	.170	.0520	22.4	14.7	1.75	1.10	43.2	43.3
100.8	.224	.125	15.21	7.51	1.24	0.93	21.0	20.8
108.2	.307	.229	11.34	3.64	0.87	.73	9.3	9.2
114.2	.358	.297	10.03	2.33	.72	.64	5.5	5.3
118.4	.394	.339	9.58	1.88	.64	.58	4.2	4.1
142.4	.534	.493	8.71	1.01	.42	.39	2.0	1.9
148.2	.556	.519	8.57	0.87	.39	.365	1.6	1.5
163.3	.602	.572	8.36	0.66	.33	.315	1.1	1.0
				n-Butylamine				
118.9	0.0315	0.014	18.50	10.05	2.52	2.15	25.2	24.6
127.8	.146	.068	17.92	9.47	1.59	1.20	26.4	26.0
137.5	.281	.191	13.26	4.81	0.98	0.79	12.8	12.7
157.2	.500	.468	9.31	0.86	.45	.43	1.4	1.3
160.2	.520	.490	9.22	0.77	.422	.406	1.2	1.1
182.5	.629	.600	9.07	0.62	.302	.287	1.1	1.0
				Di-*n*-butylamine				
129.1	0.048	0.016	25.8	13.5	2.45	1.89	37.0	37.3
137.0	.125	.110	13.9	1.6	1.31	1.29	1.0	1.3
160.4	.298	.25	14.4	2.1	0.82	0.75	4.3	4.5
254.9	.471	.45[c]	12.8	0.5	.47	.468	0.1	0.3
570.9	.608	.59[c]	12.6	.3	.313	.307	−0.04	0.4
644.6	.711	.703	12.4	.1	.208	.212	−0.2	−0.2

[a] From $\overline{\Delta H} = \overline{\Delta F} + T\overline{\Delta S}$. [b] From $-\overline{\Delta S} = \partial\overline{\Delta F}/\partial T$. [c] From desorption.

error so introduced is too small to be of any consequence.

The change in the heat content and of the free energy per mole of the adsorbate, $\overline{\Delta H}$ and $\overline{\Delta F}$, respectively, for the process

$$\text{amine (liquid)} = \text{amine (adsorbed)}$$

can be easily obtained from the present data: the former is simply the difference between the differential isosteric heat and the heat of vaporization of the amine, while the latter is given by $RT \log_e (p/p_0)$, assuming the vapors to be ideal gases. The results of these calculations are given in Table I and are plotted as functions of the amount adsorbed in Figs. 1 and 2, the dotted lines in Fig. 1 being the mean values of the heat of condensation of the amines.

These curves all have the same general features. When the amount adsorbed is low, the molal energy changes are high; at higher adsorptions, the energy changes become progressively less, $-\overline{\Delta H}$ approaches the heat of condensation and $-\overline{\Delta F}$ approaches zero. The isosteric heats for the initial portions of the isotherms are very high, being about 40 kcal. for diethylamine, almost five times its heat of condensation. This fact tends to support the view expressed in the previous paper that for these systems the adsorption may not be strictly physical.

As has been shown in the first paper, and also by the work of numerous other investigators, there is a pressure range in which the adsorption is abnormally high. This enhanced adsorption has been explained by Brunauer, Deming, Deming and Teller[4] as being due to a higher heat of vaporization of the last adsorbed layer than that of the preceding layers. This follows from their model with which they considered the capillaries as two parallel plane walls, hence the last layer is attracted on both sides. This addition energy can be calculated by Brunauer's[5] method and amounts to about 2.8 kcal. per mole for the present systems. It is to be expected that if this enhanced adsorption is caused primarily by this additional energy, then this additional energy should become liberated when the enhanced adsorption occurs, namely, at the inception of and along the hysteresis portion of the isotherms. The experimental results shown in Fig. 1, however, do not show any evidence of the presence of this additional energy. While the BDDT theory that the last layer is held more strongly than the other layers may be perfectly true, it cannot be expected to account for the enhanced adsorption, because in the capillaries the last layer practically degenerates into a line of negligible area and the additional energy postulated, being proportional to the surface area of this last layer, would be too small to make any appreciable difference in the adsorption. According to the capillary condensation theory, on the other hand, the retention of this additional amount of the amines is caused simply by the condensation of the vapors into liquids in the capillaries at lower

[4] Brauner, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

[5] Brunauer, "Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 172.

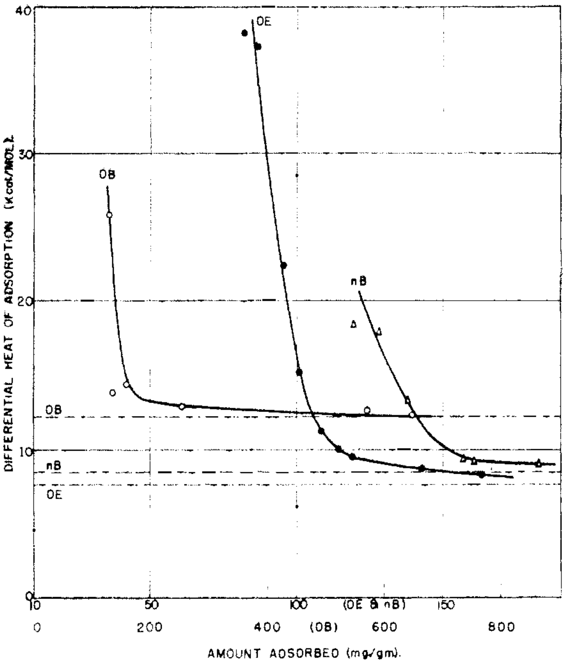

Fig. 1.

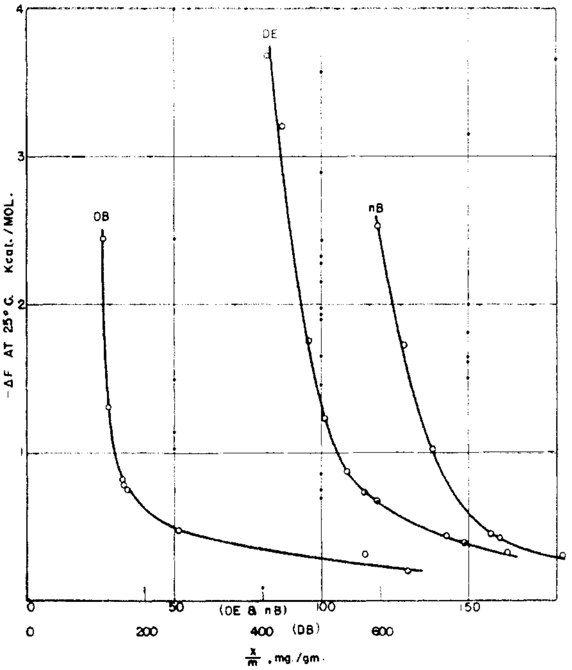

Fig. 2.

vapor pressures. The heat evolved in such a process may be expected, at the higher pressures, to approach the heat of liquefaction of the adsorbates. This was observed to be the case. The observed free energy changes can be similarly interpreted. As the vapor pressure approaches the saturation value, the adsorption is practically equivalent to the condensation of saturated vapor into liquid. This will, of course, cause no further decrease in the free energy. The fact that $\overline{\Delta H}$ and ΔF do not actually become zero but assume very small values can be easily explained by assuming the capillaries to be not uniform in size, so that even after the inception of the hysteresis some multilayer adsorption is still taking place in the larger capillaries. It appears, therefore, that the capillary condensation theory accounts more satisfactorily than does the modified multilayer adsorption theory for the energy effects observed with these systems.

When Figs. 1 and 2 are compared, it will not be noticed that the $-\overline{\Delta H}$ values are much higher than those for $-\overline{\Delta F}$. This can be easily accounted for. Due to the strong attraction between the adsorbate and the adsorbent, the polar adsorbate molecules will be oriented on the solid surface. This will cause a large decrease in the entropy of the adsorbate. Since $\overline{\Delta H}$ is negative and $-T\overline{\Delta S}$ is positive, $\overline{\Delta F}$ will be less negative and therefore has a lower absolute value than it would have if the entropy decrease were not so large. The entropy decrease can be calculated either by

$$\overline{\Delta F} = \overline{\Delta H} - T\overline{\Delta S} \qquad (2)$$

or by

$$-\overline{\Delta S} = \left(\frac{\partial \overline{\Delta F}}{\partial T}\right)_{x/m} \qquad (3)$$

The results of such calculations are also given in Table I. It will be observed that the entropy change decreases with increasing adsorption. This is to be expected as the adsorption forces are much weaker for the higher layers and consequently the orientation effect will be much less pronounced. The entropy decrease, therefore, becomes less and less and the values of $\overline{\Delta H}$ and $\overline{\Delta F}$ tend to approach each other at higher adsorption as has been observed.

When the values of the entropy changes are studied, it will be noted that the initial values are very high. In the case of diethylamine, the highest value is 89 e. u. This obviously cannot represent the energy change due to physical adsorption alone as it is even higher than the absolute entropy of the liquid amine. In the calculations it was tacitly assumed the process was

$$\text{amine (liquid)} \longrightarrow \text{amine (adsorbed)}$$

and that there was no chemical reaction between the adsorbate and the adsorbent. Since this leads to impossible values for the entropy change, the only possible explanation is that the actual process does not correspond to that postulated. It must logically follow, then, that a chemical reaction was taking place along with the physical adsorption which caused the energy values obtained, especially the $\overline{\Delta H}$ value, to be so high. These unusually high $\overline{\Delta S}$ values may, then, be considered as conclusive evidence for the chemical nature of the adsorption in these systems.

In the previous paper[3] it was suggested that the BET constant n represents not the total number of layers in the capillaries but the total number of adsorbed layers, *i. e.*, total number of layers minus the layers due to condensation. That being the case, the energy and entropy changes after 2 layers have been adsorbed should have very low values as the n values for these systems were found to be about 2. From the monolayer values for these amines, the amount of adsorbates in the first two layers were deduced to be approximately as

Diethyl	180 mg./g.
n-Butyl	220 mg./g.
Di-*n*-butyl	250 mg./g.

Inspection of the curves in Figs. 1 and 2 shows this is the case.

Free Surface Energy Changes

In a system consisting of *b* bulk and *s* surface phases the variation of the total energy is given by

$$\mathrm{d}E = \sum_{\mathrm{b}} T^b\mathrm{d}S^b - \sum_{\mathrm{b}} P^b\mathrm{d}V^b + \sum_{\mathrm{b}}\sum_{\mathrm{i}} \mu_{\mathrm{i}}{}^b\mathrm{d}n_{\mathrm{i}}{}^b + \sum T^s\mathrm{d}S^s + \sum_{\mathrm{s}} \gamma^s\mathrm{d}a^s + \sum_{\mathrm{s}}\sum_{\mathrm{i}} \mu_{\mathrm{i}}{}^s\mathrm{d}n_{\mathrm{i}}{}^s \quad (4)$$

where the symbols T, P, V, S, γ, a, μ and n are, respectively, temperature, pressure, volume, entropy, surface tension, surface area, chemical potential and number of moles, Σ_{b}, Σ_{i}, and Σ_{s} signify summation over all bulk phases, components and surface phases. From this it follows that with a single vapor in equilibrium with an adsorbent at constant temperature the familiar Gibbs equation becomes

$$-\Sigma_{\mathrm{s}} \int a^s\mathrm{d}\gamma^s = \Sigma_{\mathrm{s}} \int n^s\mathrm{d}\mu^s = \int n\mathrm{d}\mu \quad (5)$$

as the chemical potentials in the different phases are equal and each is equal to the potential in the vapor phase, and $\Sigma_{\mathrm{s}}n^s = n$, the total number of moles of vapor adsorbed by the solid.

The above equation can be utilized for the determination of the free surface energy decrease per unit area when the solid is wetted by a liquid. First, consider the solid as a non-porous substance of area a_{s}. If the temperature is much below the critical temperature and the pressure is sufficiently high, the adsorbed vapor will then condense into liquid covering the entire solid surface, provided there is no contact angle between the solid and the liquid. If the surface tension of the condensed layer is the same as that in the bulk phase, then the total change in free surface energy is

$$-a_{\mathrm{s}}(\gamma_{\mathrm{sl}} + \gamma_{\mathrm{lv}} - \gamma_{\mathrm{so}}) = \int n\mathrm{d}\mu$$

or

$$-(\gamma_{\mathrm{sl}} + \gamma_{\mathrm{lv}} - \gamma_{\mathrm{so}}) = \int n\mathrm{d}\mu/a_{\mathrm{s}} = \int \Gamma\mathrm{d}\mu \quad (6)$$

where Γ is the surface excess per unit area and the subscripts sl, so and lv denote the solid–liquid, solid–vacuum and liquid–vapor interfaces, respectively. From this relationship the adhesion tension of the solid against the liquid, defined by

$$A = \gamma_{\mathrm{so}} - \gamma_{\mathrm{sl}},$$

is then given by

$$A = \int \Gamma\mathrm{d}\mu + \gamma_{\mathrm{lv}} \quad (7)$$

The same method can be applied to porous solids. One of the differences between the adsorption by a non-porous and by a porous solid is that in the latter case the area of the adsorbing surface is continuously decreasing during the process, hence n/a_{s} no longer represents the surface excesses. Furthermore, in the capillaries liquid–vapor interfaces were created and were destroyed during the progress of adsorption. These differences, however, will not cause any complication in the determination of adhesion tension, because $a_{\mathrm{sl}} = a_{\mathrm{s}}$, and whatever area of liquid–vapor interface that may have been created during the filling process, will have disappeared completely at the saturation pressure when the capillaries become filled as the external area of the solid is negligible compared with the internal. The final result, then, is

$$-a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}}) - a_{\mathrm{lv}}\gamma_{\mathrm{lv}} + a_{\mathrm{lv}}\gamma_{\mathrm{lv}} = -a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}}) = \int n\mathrm{d}\mu$$

or

$$A = \gamma_{\mathrm{so}} - \gamma_{\mathrm{sl}} = \int n\mathrm{d}\mu/a_{\mathrm{s}} \quad (8)$$

Thus the determination of the adhesion tension of a porous solid is even simpler than that for non-porous solids. It is only when one wishes to compare the results obtained in the intermediate pressure ranges for these two kinds of adsorbents the above mentioned differences will cause any complication. In order to simplify the calculation and interpretation, the following *hypothetical process* may be substituted for the actual process. Let the porous solid be spread out into a plane surface of the same area as that on which adsorption takes place until a layer of the condensed liquid appears. Assume that the surface tension of the condensed layer decreases with increasing adsorption and that it reaches zero value at the maximum adsorption, *i. e.*, when the pressure reaches the saturation value. As far as the total energy effects are concerned, the actual and the hypothetical processes are equivalent as the following comparison will immediately show:

The actual case: $-a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}}) - 0\gamma_{\mathrm{lv}} = -a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}})$

the hypothetical case: $-a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}}) - a_{\mathrm{s}}0 = -a_{\mathrm{s}}(\gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}})$

The advantages of the hypothetical process are that it is not necessary to know how the area of the adsorbing surface changes with adsorption, and a single integration is sufficient to evaluate the energy changes, because in this process the change in the available surface energy is, by hypothesis, solely due to the decrease of interfacial tensions. The individual values of the integral $\int \Gamma\mathrm{d}\mu$ at different pressures will then correspond to the energy changes per unit area. If one wishes to convert these hypothetical into the actual values, it can be accomplished by the method indicated in a later section.

In order to evaluate $\int \Gamma\mathrm{d}\mu$ a graphical method was used in conjunction with the usual simplifying assumptions, *i. e.*, identifying $\mathrm{d}\mu$ with RT d $\log_e p$, and Γ with x/ma_{s}, a_{s} being 320 m.²/g. in the present case. Both of these simplifications will undoubtedly introduce some inaccuracies into the calculations, but it is believed that they will not be serious, as the pressures are fairly low, the highest being 238 mm. for diethylamine. The results of these calculations are given in Table II and plotted *vs.* relative pressures in Figs. 3 and 4, the latter being the log–log plot of Fig. 3. From these calculations the adhesion tensions of silica gel against the three amines at 25° are found to be

Diethylamine	100 ergs/sq. cm.
Di-*n*-butylamine	91 ergs/sq. cm.
n-Butylamine	119 ergs/sq. cm.

TABLE II

FREE SURFACE ENERGY CHANGES ON SiO_2 GEL AT 25°

	Diethylamine		Di-*n*-butylamine		*n*-Butylamine	
p/p_0	$\Gamma \times 10^{10}$ (moles/ sq. cm.)	$-\Delta\gamma$ (ergs/ sq. cm.)	$\Gamma \times 10^{10}$ (moles/ sq. cm.)	$-\Delta\gamma$ (ergs/ sq. cm.)	$\Gamma \times 10^{10}$ (moles/ sq. cm.)	$-\Delta\gamma$ (ergs/ sq. cm.)
0.01	3.89	31.9	3.09	32.0	5.04	34.6
.02	3.98	38.5	3.11	37.4	5.16	43.2
.03	4.02	42.5	3.16	40.5	5.24	50.5
.04	4.07	45.0	3.18	42.7	5.29	54.5
.05	4.10	47.5	3.21	44.5	5.36	56.9
.10	4.27	54.8	3.38	50.2	5.64	65.0
.15	4.36	59.1	3.55	53.7	5.70	70.2
.20	4.53	62.3	3.72	56.3	5.89	74.4
.25	4.70	64.4	3.88	58.4	6.02	77.7
.30	4.91	67.0	4.10	60.2	6.19	80.4
.35	5.09	68.8	4.34	61.8	6.32	82.8
.40	5.38	70.6	4.63	63.3	6.45	84.7
.45	5.73	72.3	5.06	64.7	6.62	86.8
.50	6.15	73.8	5.60	66.1	6.92	88.8
.55	6.70	75.3	6.64	67.5	7.30	90.4
.60	7.39	76.7	8.24	69.1	8.07	92.0
.65	8.55	78.2	10.86	71.0	8.96	93.7
.70	10.5	79.8	14.49	73.3	10.4	95.5
.75	13.2	81.9	19.3	76.2	12.5	97.4
.80	20.9	84.3	21.4	79.1	20.3	100.0
.85	31.0	88.3	21.5	82.3	34.2	103.9
.90	35.2	92.3	21.6	85.1	36.3	109.2
.95	35.4	95.9	21.65	88.1	36.6	113.9
1.00	35.5	100.0	21.7	90.9	36.8	118.5

The absolute values in the above list may be in error by as much as 10%. In addition to the uncertainty inherent in the BET method for the surface area determination, the other difficulty is to locate the linear portion of the adsorption isotherms in order to evaluate the integral from zero to the lowest pressure actually measured. As the initial rise of the isotherms of these amines was extremely rapid, it was not possible to evaluate the initial slope very accurately, and an error of about five ergs may result from this source. The relative values, however, are more reliable. It may be mentioned that these three systems probably represent the extreme cases. With other systems, alcohol–silica, for example, the errors due to integration would be much smaller.

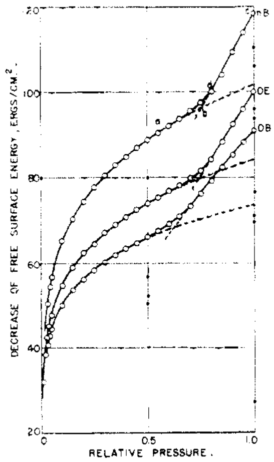

Fig. 3.

In order to obtain reliable results by this method, the primary requirements are that the vapors must have been condensed into liquids to fill up the capillaries completely and that these liquids must have the same properties, especially the surface tension, as that in the bulk. Questions covering both these points can be answered from an inspection of the curves in Fig. 3. All these curves have the same general features. At low pressures the surface energy drop is very rapid; at medium pressures the rate of decrease slackens. This portion of the curve is entirely analogous to those curves depicting the variation of surface tension of water with the concentration of capillarily active substances. As the pressure becomes still higher, the rate of energy drop becomes large again until the saturation pressure is reached. This second drop has no analog in the liquid–vapor systems. The logical explanation of this second drop is to assume that there is a layer of liquid condensed on the solid surface within the capillaries. As more vapor condenses, the area of this liquid surface will, of course, decrease, or, the surface tension decreases according to the hypothetical process, hence the available surface energy also decreases. If there is no condensation of the adsorbed vapors, then it is impossible to explain this second drop. Comparison of the pore volume of the gel with the volume of the liquid condensed shows that the capillaries are completely filled up.

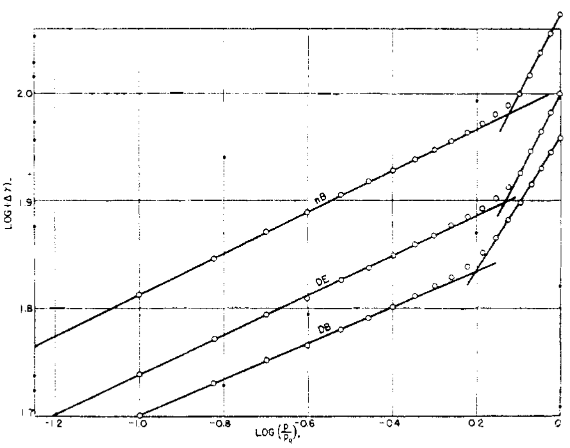

Fig. 4.

The surface tensions of the condensed liquids can also be estimated from these curves. If the radii of the capillaries are the same, then condensed films should be formed on all the walls at the same time. Since the second energy drop has been attributed to the liquid film, then for gels with uniform radii the $-\Delta\gamma$ *vs.* p/p_0 curve should follow oabc of Fig. 3 where b is the interaction of oa and dc produced and can be accurately located from Fig. 4. As stated previously, the ordinates of the curves in Fig. 3 represent the change of available surface energy per unit area, the difference between the ordinates b and c is then the surface tension of the liquid in the capillaries. Accepting this explanation, the surface tension of these three amines can be read off from Fig. 3 as

	From curves	Experimental
Diethyl	20.0 dynes/cm.	19.1 dynes/cm.
Dibutyl	22.7 dynes/cm.	23.6 dynes/cm.
n-Butyl	22.1 dynes/cm.	22.9 dynes/cm.

Considering all the uncertainties and assumptions involved in the calculation, the agreement between the estimated and the experimental surface tensions is satisfactory. As these surface tensions are close together, it is desirable to be able to check the premise by using some other system for which the surface tension value is quite different from those listed above. For this purpose the system water vapor–silica gel investigated by Anderson[6] can be used. It was found for this system the simple BET equation is applicable to about $p/p_0 = 0.3$. From the v_m value, the number of molecules required to form a complete monolayer, so obtained, the specific area of Anderson's silica was estimated to be 434 sq. m./g. using Livingston's[7] value, 10.6 sq. Å., for the molecular area of water on silica. Using the same procedure as before Fig. 5 was obtained for water. From this figure the surface tension of water at 15° was found to be 73, the accepted value being 73.5. While this close agreement may well be fortuitous, it does lend support to the above argument.[8] Thus it is shown that the surface tensions of liquids in the capillaries do have practically the same values as in bulk, at least for such pore size as for this silica gel.

The actual curves, however, follow adc instead of abc. This can be easily understood. The silica gel used contains, of course, pores of various sizes. Since the condensation of the vapor depends on the pore radius, it must start in the smaller pores before point b is reached. As the rate of change of $-\Delta\gamma$ with respect to pressure is highest at the inception and lowest at the end of the process, the energy drop due to the change of surface energy of the film is greater than that due to the similar change of the solid–liquid interface. Therefore, the course of the actual curve adc lies above the idealized curve abc. This also explains why the dibutylamine curve starts to deviate from its normal course at a lower relative pressure, because the reduction of the pore radius depends on the size of the adsorbate molecule and dibutylamine has the largest size among the three amines.

According to the above argument the choice of point b to indicate the inception of condensation of vapors is equivalent to using the average radius in place of the actual radii. Even though the procedure adopted to locate point b, the intersection of the two logarithmic curves, seems reasonable, it would be very desirable if it were possible to check the premise by some other methods. This can be accomplished by calculating the area of the liquid surface in two ways only one of which involves point b. The change of surface energy due to the change of surface area is given by

$$\int_{a_1}^{a_2} \gamma \mathrm{d}a = RT \int_{n_1}^{n^2} \log_e \frac{p}{p_0} \mathrm{d}n \qquad (9)$$

When the $-\Delta\gamma$ *vs.* p/p_0 curve starts to deviate from its normal course, it indicates the appearance of the liquid phase. This contention is supported by the fact that the pressure corresponding to point a agrees closely with that at the inception of the hysteresis loop. This, then, fixes the lower limit of the right hand integral, whose upper limit is of course the number of moles adsorbed at the saturation pressure. The value of the first integral is simply $-a_{lv}\gamma_{lv}$, as the surface tension of the condensed liquid has been shown to have the same value as that in the bulk, hence presumably constant. Therefore, after the second integral has been evaluated, the surface area of the liquid layer can be obtained. From the pressure corresponding to point b, p_b, the amount of vapor adsorbed can be read off from the adsorption isotherm. By assuming the capillaries to be circular, the thickness t and the area of the liquid layer can be calculated from the

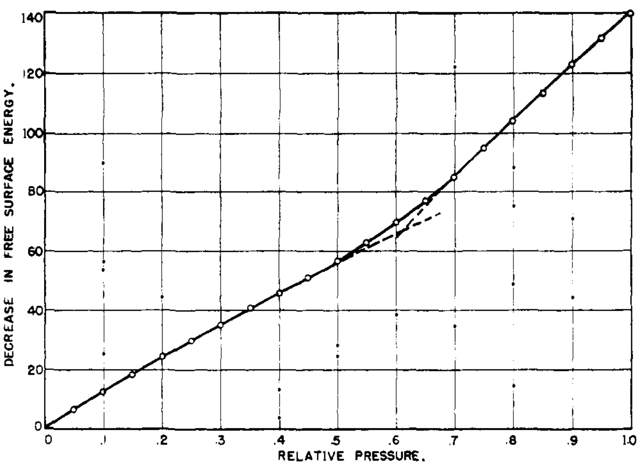

Fig. 5.

$$\frac{\text{area of layer}}{\text{area of solid}} = \frac{\bar{r} - t}{\bar{r}} = \left[I - \frac{\text{wt. adsorbed at } p_b}{\text{total wt. adsorbed}}\right]^{1/2} \qquad (10)$$

where $\bar{r}$ is the average radius of the capillaries. The values of the areas of the condensed liquid layers obtained by these two methods are listed below:

	From Equation (9)	From Equation (10)
Diethylamine	2.49×10^6 sq. cm.	2.55×10^6 sq. cm.
Dibutylamine	2.24×10^6 sq. cm.	2.42×10^6 sq. cm.
n-Butylamine	2.53×10^6 sq. cm.	2.52×10^6 sq. cm.

The agreements are satisfactory. Equation (10) may be further checked in another way. The thickness of the monolayer can be calculated from Γ_m, the number of moles of the adsorbate required to form a complete monolayer on a unit surface. The same quantity can also be obtained from equation (10). For *n*-butylamine Γ_m was 5.1×10^{-10}. From this, the thickness of the monolayer was found to be 5.08 Å., which agrees satisfactorily with 5.04 Å. obtained from equation (10).

As mentioned previously, the ordinate of point b represents $(-\gamma_{sl} + \gamma_{lv} - \gamma_{so})$, *i.e.*, when a solid of unit area is in contact with a layer of liquid of the the same area. In the capillaries, however, a_{lv} is smaller than a_s. For the present systems the above calculations showed a_{lv} is only 79% of a_s. Therefore, the actual energy change corresponding to point b for *n*-butylamine, say, is 100 instead of 96 as indicated in Fig. 3. The actual values at other points, of course, can be obtained in similar manner.

Finally it may be noticed that even though the present method should be a general one for the determination of adhesion tension of porous solids against liquids, it does not distinguish between chemical and purely surface energies. In the present case, the values obtained include both kinds of

---

[6] Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

[7] Livingston, THIS JOURNAL, **66**, 569 (1944).

[8] Recent work in this Laboratory on fifteen other systems with various solids and liquids whose surface tensions range from 9 to 30 dynes/cm. also substantiates this view.

energy changes. It may be mentioned, however, that with systems such as silica–alcohols, or cellulose–nitrogen, where the possibility of chemical reaction is much smaller, exactly the same type of $\Delta\gamma - p/p_0$ curves have been obtained.

Summary

1. Isoteric heats of adsorption of three aliphatic amines by silica gel were determined by means of adsorption isotherms obtained at 25° and at 40°.

2. The change in the heat content $\overline{\Delta H}$, the free energy $\overline{\Delta F}$ and the entropy $\overline{\Delta S}$ per mole of adsorbate were determined.

3. The isosteric heats and $-\overline{\Delta S}$ obtained for the initial stages of adsorption were so high as to indicate that adsorption in this range is not strictly physical.

4. From energy and entropy considerations it appears that at high relative pressures (*i. e.*, over the range represented by the hysteresis portions of the isotherms) condensation of vapor occurs within the capillaries.

5. From the Gibbs equation interrelating surface area, surface tension, surface excess and chemical potential, it becomes possible, with adsorption data alone, to determine the free surface energy change which occurs when unit area of solid (adsorbent) is wetted by a liquid. By definition this energy change represents the adhesion tension value of the system. The method for the determination of adhesion tension is particularly suited for use with porous solids.

6. Further evidence was obtained to substantiate the view that the surface tension of liquids in capillaries as small as exist in silica gel have practically the same values as when in bulk.

7. Through adsorption studies it is possible to determine the areas of the adsorbed liquid layers and also the thickness of the adsorbed liquid layer.

ANN ARBOR, MICHIGAN RECEIVED MAY 24, 1950

[CONTRIBUTION FROM RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, CONTRACT NO. W-7405-ENG-48]

Heats of Formation of Sodium Potassium Alloys[1]

BY RALEIGH L. MCKISSON AND LEROY A. BROMLEY

Introduction

Joannis[2] has measured heats of formation of the sodium potassium alloys by the difference of the heats of solution of the alloys and the elements in water. Bichowsky and Rossini[3] have corrected these values by using more accurate data on the heat of solution of the elements. Kawakami[4] has measured the heats of formation by noting the temperature change upon direct mixing of the elements in a calorimeter. The results of these authors are in such disagreement (see Table II) that further investigation is imperative. The results of the preliminary experiments in this Laboratory are reported herein.

Method, Procedure and Results

The method of direct addition of reactants was chosen because an inert atmosphere "dry box" which facilitated handling of large quantities of molten metals was available. The argon atmosphere in the dry box was maintained oxygen and water free by a clean molten sodium surface over which the argon atmosphere was continuously blown except during actual experiments. The quantities of sodium or potassium used in the measurements varied from two to three moles total. All temperatures were measured with the same mercury in glass thermometer graduated in degrees.

The procedure consisted of recording the temperature of the reactant in the calorimeter vessel when it attained a constant value, reading the temperature of the addendum with the same thermometer, and finally reading the temperature of the mixture after stirring vigorously with the thermometer. The equilibrium temperature was attained in about 15 seconds.

The calorimeter used for the NaK measurements consisted of a thin-walled molybdenum container. Heat capacities were calculated using the data of Kelley[5] and the total weight of molybdenum. A 0.5 pint dewar was used as the calorimeter for the Na_2K and the NaK_2 measurements. Its effective heat capacity was measured by the method of mixtures at two melt heights and a linear relation between heat capacity and melt height was assumed. Corrections were made for the temperature drop in the addendum during pouring, and for the temperature drop of the dewar while equilibrium was attained. The former correction was about −3°, the latter, −1°.

Determinations were made at a number of different temperatures for the alloy NaK so that a value for ΔC_p of the reaction could be obtained. The least squares method was used to fit a straight line to the experimental points. The reaction is

$$\mathrm{Na(l)} + \mathrm{K(l)} \longrightarrow \mathrm{NaK(l)}$$

The equation, in cal./mole and °K., is

$$\Delta H_f = 42 + 0.86\, T$$

The determinations on the alloys NaK_2 and Na_2K were made using NaK and adding the required element. Heat effects were measured and combined with the ΔH_{f298} of NaK, and the C_p data of Kelley[5] to evaluate ΔH_{f298} for the products. Table I shows the values of ΔH_{f298} found in the various runs.

---

[1] Based on University of California Radiation Laboratory Report UCRL 671, April 17, 1950.

[2] Joannis, *Ann. Chim. Phys.*, [6] **12**, 358 (1887).

[3] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[4] M. Kawakami, *Tohoku Imperial University Science Reports*, Series I, **16**, 915 (1927).

[5] K. K. Kelley, U. S. Bureau of Mines, Bulletin No. 476 (1949)