

Citation:

Kuenen, J.P. & Visser, S.W., The virial-coefficient B for normal butane, in:
KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 350-355

Physics. — "*The virial-coefficient B for normal butane.*" By Prof.
J. P. KUENEN and S. W. VISSER.

(Communicated in the meeting of September 27, 1913).

Determinations of the vapour density of normal butane have enabled us to calculate the virial-coefficient B in the empirical equation of state as established by KAMERLINGH ONNES¹⁾. In the course of these calculations anomalies appeared which may be explained by the presence of a small quantity of a lighter admixture: a confirmation of this supposition was obtained by determinations of the boiling point and from the critical temperature.

The vapour density was determined by weighing. For this purpose a glass bulb of about .4 litre was used, provided with a stopcock and ground joint by means of which it could be connected to a butane-reservoir, a mercury pump, and an open mercury manometer.






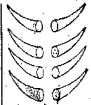
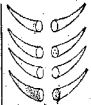





The volume of the bulb was determined by weighing with air. First the weight of the bulb was determined after having been exhausted as completely as possible by the mercury pump. In all the weighings a tarra-bulb of about the same external volume was suspended from the other arm of the balance: the reading was not taken until the equilibrium had become constant.

The pressure of the air and afterwards of butane was first of all taken equal to the atmospheric pressure, the temperature being that of the room. For this purpose a tube some metres long with a stopcock was attached to the filling-apparatus. The gas was admitted to a pressure of about 1 m.m. above the atmospheric: by opening the tap at the end of the long tube for a moment, the excess pressure could be let off without appreciable change of temperature and without fear of outside air penetrating into the bulb. Immediately after closing the bulb the temperature and pressure were read. The bulb was then weighed. In filling the bulb with butane vapour it was three times washed out with the vapour and exhausted.

The barometric pressures were reduced to 0° and in the weights at temperatures above 0° a correction was applied for the expansion of the glass.

In the same manner a determination with butane was made at 0°, the bulb having been kept in ice for at least half an hour. During the operation the butane-reservoir was also placed in ice to

¹⁾ Leiden Comm. Suppl. 23; § 36; p. 114, sqq.

NUMBER OF EXPERIMENT	L E S I O N	VESTIBULAR ROOT	POSTER. LONGITUDINAL FASCICLE				CIRCUS MOVEMENT	DURATION	ROLLING MOVEMENT AND ALLIED CONDITIONS	DURATION	FASC. DEITERS ASCENDENS		AREAL OF P.L.B. AND FASC. DEIT. ASC.	REMARKS ABOUT OTHER DEGENERATIONS	
			Ascending		Descending						Ascending	D.			
			L	R	L	R									L
GROUP I. Direct lesion of the Vestibular nerve.															
235.03	Acoustic-vestibular region on R. side	R.: Wounded, entirely degenerated.	Little degeneration L > R				Head turned to R.	25 days	Rolls and falls to R.; lies on R. side	28 days	Degenerated			Degeneration on R. side: Tr. vestibulo-ocular; descending Ramus V and VIII; V and VIII root; corp. trapezoid, striae acust. (Moskowsk, Held), Nuc. Delters, Corp. restit.; anterior and med. crus, nuc. dentat.	
Rabbit V	L.: Exstirpation of so called flocculus	L.: degenerated	0	0	0	0	0	0	Head rotated and bent to L.	20 "	0	0		N. acust. and corp. trapezoid, free of degeneration. Vestibular fibres followed up in: Mus. Ram. desc. VIII, Nuc. trapezoid, dorsal colliculus and nuc. test. Middle third part of L. Crus ant. cerebelli.	
42	R.: Acoustic-vestibular cut	R.: entirely degenerated	0	0	0	0	0	0	Vehement rolling to R. with eye-ball rotation	75 "				R: Corp. restiforme, corp. trapezoid, striae acustic. Held. On both sides R > L: descending V and VII root and medial and lateral fillet.	
67	Destruction R. N. Vestib. and ganglion ventrale; proximal end of incision in lateral part of Fasc. Delt. asc.	R.: destruction	0	0	0	0	0	0	0	Vehement rolling to R. with eye-ball rotation	20 "				R: Corp. trapezoid, corp. restit. (moderately); nuc. Bochterew (?); nuc. test. nuc. central and crus ant. Ram. desc. V and VII free of degeneration.
GROUP II. Indirect, intramedullary, slight lesion of N. vestibularis, by shifting of cranial contents or vicinity of a malacia head.															
107	R.: Nuc. commiss. post., corp. quad. ant., corp. gaseic. lat.	L.: little degeneration (oral part)	0	0	0	med. dorsal	Circus to R.	8 days	Head rotated to L.	8 days	0	0		R: Descending tract lateral to P.L.B. (Probst, Besta); nuc. niger (ventro-lateral part) and Fasc. intertrillo-spinal (slight); L.: Subrospinal and pyram. tract; nuc. triangul.	
108	R.: lateral to nuc. commiss. post. (nuc. interstitial) cavity	L.: middle and proximal part degenerated	0	0	0	fasc. inter-trillo-spinal	L	1 day	Tendency to fall to L.	9 "	0	0		R: Mesencephalic V root, corp. quad. ant., lemniscus lat., tract. opt., commissura post. L.: Monakow's, pyramidal and tecto-spinal tract, nuc. triangul.	
109	Incision from L. ganglion haben. till R. corp. quad. ant.	L.: little degeneration (oral part)	0	0	0	little	R	1 "	0	0	0	0		L: Tecto-spinal (total), Pyramidal tract (diffuse) owing to lesion of medial part of caps. int. R.: Mesencephalic V root and commiss. post.	
134	R.: Exstirpation of ant. lob. cerebell. (nuc. glob. nucleus)	L.: little	some fibres	0	0	0	Tendency to L.	3 days	Rolls over L. side	1 day	0	0		R: Retrograde degeneration in area of spinocerebellar tracts and corp. restiforme; medio-lateral part of crus ant. L.: floccular bundle (Rosenfeld-Thomson).	
113	R.: Nuc. triang. VIII, nuc. intravest. and medialis groups (Fasc.)	R.: ventral part	lateral	0	med. ventral	lateral	Circus to R.	8 "	Head rotated to R.	8 days		lateral		R: Moskowsk's, vestibulo-spinal bundle, corp. restit., motor. V nuc. lemniscus, crossing of cerebellar crura (ventral part) lemniscus med. and Probst's commissure. L.: Pyramid. tr.	
116	R.: Dorsal magnocellular part of nuc. Delt. (also med. group and nuc. triang.)	R.: oral part	little	0	med. ventral	lateral	R	1 day	Falls to R.	7 "	0	0		R: Vestibulo-spinal and pyram. bundle, striae Moskowsk, rubro-spinal bundle, motor. V root, subot. reticul. lemniscus, medial fillet.	
95	R.: Nuc. Bochterew and nuc. bacilli pontis sup.	R.: oral part	0	0	0	lateral-ventral	L	7 days	0		0	0		R: Rubro-spinal b.; corp. trapezoid, (oral part); descend. V nuc.; V roots (not and sens) and medial fillet. (Crus cerebelli ant. posterior and lemniscus weakened. Deiters nuc. free.)	
Rabbit I	L.: Commiss. post. and nuc. interstitialis (v. Valkenburg) ?	?				diffuse	Splice bent to L.	4 "	Falls to R. with eye-ball rotation	6 "				Weigert-Pal stain; L.: Nuc. Gueden atrophied. A.L.3. atroph. 64 medial region. Also mes. fillet. Weigert-Pal stain.	
GROUP III. Exclusive lesion of vestibular nuclei. Under this head, strictly taken probably no one animal can be presented, except VII. Practically however may be regarded as such 113, 116, and 65, because the slight degeneration of the vestibular root can hardly be considered responsible for the symptoms. Also 99, 94, and 93, and the slight lesion in the vestibular region (146 and 189) may be consulted.															
VIII	R.: Cyst in caudal part of Ram. desc. nuc. VIII	0	L > R	little	L > R	little	0	0	Rolls to L.; head and eyes rotated to L.	2 d.; 4 d.				R: Rubro-spinal and vestibulo-spinal b.; fibre ariformis int., desc. V nuc., lateral X nuc., corp. restit., striae acust. (Mon.), crus ant. and Govers b. L.: medial fillet.	
99	L.: Ramus desc. nuc. VIII, nuc. triang. and Bochterew full of degenerated fibres.	0	0	little	0	little	L	21 days	Head little rotated to R.	9 days				L: Vestibulo-spinal b.; lateral fillet. Most of ascending P. L. B. fibres stop in pons.	
146	R.: Sagittal lesion: caudal medial of nuc. Delters and transection of cord (P 4)		little		little	little	Some tendency to walk to L. side	some days	Same tendency to fall to L.	some days				R: Vestibulo-spinal b.; Govers and Flechsig b.; hilus olivae and medial fillet; corp. trapez. R. and L. Goll's tract L.: Pyram. tr.	
158	L.: Sagittal lesion: Delters complex completely cut off caudally and L. frontal pole removed.	R. and L.: little	Diffuse, little	lateral	lateral	medial	0	9 days	Falls to R.	11 days		medial part		R: Middle part of nuc. V desc.; nuc. corp. quad. post. R. and L. corp. trapezoid, hook bundle, crus med. cerebelli. (L > R) L.: Pyram. and direct vestibulo-spinal b., nuc. dent. (L. crus ant. free), lemn. med. and nuc. lemn. lat.	
GROUP IV. Lesion of longitudinal fibres, ascending from vestibular complex, between nuc. VI and nuc. IV, except 114 and 159.															
92	Both P. L. B. + L. Fasc. Delt. asc.	L. nuc. Bochterew cut off from raphe.	Total	Total	Total	Total	0	0	Falls to L.; eyes rotated to L.	4 d.; 12 d.	Degenerated			L: Rubro-spinal tract; nuc. IV, R. and L.: Nuc. Delters and Bochterew, in their oral parts, cut off from raphe; lateral fillet. R.: crus med. cerebelli.	
20	Both P. L. B. + R. Fasc. Delt. asc.		Total (one oral part)	Total and strong	Total	Total	Circus to R.	9 days	Head rotated to R.	8 days	Medial part			Hemorrhage on L. P. L. B. R. and L.: Crus cerebelli ant. posterior (deep layer). R.: crus cerebelli ant. (medial part) L.: lateral fillet.	
23	Incision in R. crus cerebelli. ant. and F. Delters asc.	Lesion of R. nuc. Bochterew and triangularis	0	little	0	little	Tendency to walk to L.	6 "	Rolls to R.; falls to R.	8 d.; 22 d.	0			R: F. vestibulo-spinal, corp. restit., nuc. globosa, crus cerebelli med. and ant.; format. reticul. pontis and mesencephalic V root.	
62	Incision in R. crus cerebelli. ant. and F. Delt. asc.					little, lateral	0	0	Rolls to R.	6 days				R: Monakow's and Govers' bundle; nuc. test. crus cerebelli med. and ant. (with descending collicularis, Thomas, Protsh. Hemorrhage in nuc. med. V.	
209	R.: Fasc. Delters asc., near nuc. IV						0	0	Rolls to R.	5 "				R: Motor and mesencephalic V root; rubro-spinal and lateral part of pyramidal tract; lateral fillet. R. and L.: nuc. test. and middle third part of descending V column.	
79	Rabbit (Kolnatskaya) R.: Fasc. Delt. asc. (lateral part)						0	0	Head rotated to R. (thin to L. and upward)	4 "	0			R: Govers' and rubro-spinal bundle; crus cerebelli ant. and med. (oral part); nuc. of P. L. B. contains many degenerated cells; also both IV nuclei and L. nuc. angularis.	
Series III V. 1	(Besta) Cat. Ablation of L. cerebellum		Degenerated	moderately (del) total	Total	Total	0	0	Rolls with locomotion to L.	4 "	Degenerated			R: Middle (superficial layer) and anterior (total) crus cerebelli; nuc. Bochterew (?). R. and L. hooklike bundle. L. nuc. reticulata.	
114	Both P. L. B., oral to IV nuc. and Wernicke's commissure		0	strong (lateral)	little	Ventro-medial	Circus to L.	9 "	0	0	Total destruction			R: Rubro-spinal and lateral part of pyramidal bundle, medial fillet, Wernicke's commissure; medial part of corp. quad. post. L.: nuc. rab. and dorsal parts of III nuc.	
135	Extensively R. P. L. B. and substantia reticularis		0	strong (lateral)	little	Ventro-medial	Circus to L.	9 "	0	0	Total destruction			R: R. and L.: Middle crus cerebelli rhythm prof.; proximal part of corp. trapezoid and olivae sup. (oral to VI nuc);	
68	R.: Lateral half of pons. Hemorrhage on R. Fasc. Delters asc.	Proximal part of R. vestibular root	Total	little	Total	little	Circus to R.	8 "	Lies on L. side	last days	Middle part			R: Rubro-spinal, Govers' and medial part of pyramidal tract, descending V and VIII nuc.; corp. restit. (lateral part); ant. and middle crus cerebelli. Oral parts of Delters and Bochterew nuclei within malacia.	
91	L.: P. L. B. and medial part of Fasc. Delt. asc.	On R. side a little	Total	little	Total	little	Circus to R.	8 "	Falls on R.; lies down on R. side	14 days				R: Pyramidal bundle, nuc. triangul., crus ant. cerebelli (moderate); L.: Rubro-spinal and hooklike bundle. Wernicke's commissure. Paracetic infection.	
221	8 figures in proximal part of vestibular nuclei and L. Fasc. Delters asc.		Lateral	0	Moderate	little	Head bent to L.	1 day	Tendency to lie down on L. side	15 "				R: Crus cerebelli ant. (with descending collicularis — Thomas, Protsh.) R. nuc. IV full of degeneration.	
5	(Economo and Karplus) Cat. R.: Pes pedunculi and P. L. B.					Medial	L	5 days	Falls to L.	9 "				R: Pyramidal and mesencephalic-olivary tract; crus ant. cerebelli ant. lemniscus. — Both rubro-spinal tracts.	

Underlined in this table are the tracts, degenerated, which — after our present knowledge — probably determine the functional disturbances (equally underlined).

1) Proceedings Royal Dutch Academy. 1912. P. 1113.
2) Journal f. Psychologie u. neurologie XVI. 1910. Bdz. 93.
3) Archiv. f. Psychiatrie. Vol. 50. 1912. P. 373.
4) Archiv. f. Psychiatrie. Vol. 48. 1916. P. 311.

prevent distillation of liquid into the bulb. After the weighing the weight of the empty bulb was determined a second time as a test.

Subsequently determinations at room temperature were made at pressures of $\frac{1}{2}$ and $\frac{1}{4}$ atm. The pressure was in this case read on the mercury-gauge.

It appeared necessary to determine the contraction of the bulb by the diminution of the internal pressure. For this purpose the weight of air contained in the bulb at a pressure of $\frac{1}{4}$ of an atm. was measured.

Finally two weighings were made with butane-vapour at 0° and at $\frac{1}{2}$ and $\frac{2}{3}$ of an atm.

MEASUREMENTS ¹⁾.

Empty bulb. The tarra-bulb + 8 grammes made equilibrium with the empty bulb + .84036 grms. A later weighing gave .84033, a third .84036. The mean of these is .84035. This weight is in error by an amount x , owing to the change of the external volume by exhaustion.

Bulb with dry air. At $18^\circ.58$ and 76.738 cms. the weight of the air was found to be .47370 grms; a second weighing gave .47735 grms. at $16^\circ.88$ and 76.805 cms. For the weight at 0° and 76 cms. they give .5009 grms and .5014 grms. the mean of which is .5012 grms. This figure has to be increased by the amount x mentioned above.

Bulb with dry air at lower internal pressure. At a pressure of 26.816 cms and a temperature of $16^\circ.71$ the air weighed .16596 grms. The weight of the air contained in the bulb at 0° and 76 cms would have been .49899 grms. It is easily proved, that the error of this figure owing to the change of external volume is approximately equal to x . The difference between .5010 and .49899 is therefore independent of x and represents the diminution of weight due to the diminution of internal volume at the lower pressure: as the diminution may be taken proportional to the change of pressure, it follows that the diminution of weight for 1 atmosphere would be .00333 grms. The external change of volume being approximately equal to the internal change, this latter weight is equal to the correction x . The weight at 0° and 1 atm. is thus $.5012 + .0033 = .5045$ grms. From this weight the volume is found by dividing by the normal density of air. The measured weights of butane have

¹⁾ The calculations as given here differ slightly from those in the Dutch edition owing to a correction which had been overlooked.

also to be corrected by amounts proportional to x and to the pressure expressed as a fraction of 76 cms.

Bulb with butane vapour.

The following table gives the results of the 6 weighings.

	Temp.	Pressure	Weight.	Weight corrected.	Volume.
I.	16°.63	76.08 cm.	0.98219 Gram	0.98513	390.1 ccm.
II.	0 .00	75.68	1.04400	1.04733	390.1
III.	21 .02	40.42	0.50339	0.50469	388.9
IV.	19 .94	18.57	0.22935	0.23016	388.1
V.	0 .00	23.48	0.31244	0.31347	388.3
VI.	0 .00	48.89	0.66184	0.66398	389.2

EMPIRICAL REDUCED EQUATION OF STATE.

The equation of state was taken in the form (Comm. Leiden, Suppl. 23)

$$pv = A \left(1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} \right) (1)$$

where p is the pressure in atmospheres at 45° latitude, v the volume of 1 gramme expressed in the theoretical normal volume as unit, further :

$$A = RT; \quad B = \frac{RT_k}{p_k} \mathfrak{B}; \quad C = \frac{R^2 T_k^2}{p_k^2} \mathfrak{C}; \text{ etc.}$$

\mathfrak{B} , \mathfrak{C} , etc. represent the "reduced virial coefficients", quantities which depend on T only and must be equal for different substances, except for small individual deviations.

D and the subsequent coefficients may be neglected for pressures smaller than $\frac{1}{2} p_k$.

By introducing p as the independent variable instead of v equation (1) assumes the form.

$$pv = RT \left(1 + \frac{B}{RT} p + \frac{C - B^2}{R^2 T^2} p^2 \right) (2)$$

The theoretical normal volume of pure butane is

$$22412 : 58.08 = 386.0$$

where 22412 is the normal volume of one gramme-molecule and 58.08 the molar weight of butane. When the constants were calculated on this basis, large deviations from the reduced equation of state were found. This finds a ready explanation in the fact, that

the butane was not absolutely pure. It seemed therefore preferable to treat the theoretical normal volume as an unknown quantity and deduce it together with the other constants from the observations. It was for this purpose, that the above weighings at 0° at three different pressures were made.

Substituting in (2) p_i , v_i and p_o , v_o respectively and dividing the two resulting equations, we obtain the relation

$$1 - \frac{p_i v_i}{p_o v_o} = \frac{B}{RT} (p_i - p_o) - \frac{B^2}{R^2 T^2} (p_i - p_o) \left\{ p_i + \left(1 - \frac{C}{B^2} \right) (p_i + p_o) \right\}. \quad (3)$$

In this equation we may take for v_i and v_o the volumes of 1 gramme in ccm. The term containing C is of minor importance: C may therefore be calculated with sufficient accuracy from the reduced coefficient \mathfrak{C} , which is known from measurements on a number of other substances.

From equation (3) was found $B = -.0430$

In the same manner the second and sixth weighings gave $B = -.0431$; as the mean was taken .0431.

The theoretical normal volume of the butane used may now be calculated from equation (2): it becomes 388.1.

The difference of this figure from the value for pure butane (386.0) gives an indication as to the amount of the impurity: it points to the presence of a lighter admixture. The difference is .5%.

Using the normal volume found in this manner we may now deduce the virial coefficients B in the measurements at other temperatures.

t	B	B calculated.
0°	— .0431	— .0465
16.63	381	393
19.94	371	382
21.02	359	376

In the last column are given the values of B , as calculated from the mean reduced virial coefficient \mathfrak{B} for a number of substances. The correspondence is satisfactory considered the degree of accuracy of the method by which B was here determined. An error in the fraction on the left side of equation (3) appears in B one hundred times enlarged; an error of 5% in B corresponds to an error of observation of $1/2000$.

Moreover a complete correspondence can in any case not be expected, as the equation of state is after all only an approximation

owing to the mutual deviations of the various substances with regard to the law of corresponding states. This is shown by the following table containing various values of \mathfrak{B} .

Reduced temperature .644.		
mean reduced virial-coefficient $\mathfrak{B} = -1.12$.		
	t	\mathfrak{B}
ammonia ¹⁾	-12° C.	-1.22
methyl chloride ¹⁾	-5	-0.961
isopentane ²⁾	23.7	-1.02
n. butane ³⁾	0.0	-1.04 .

Test of the impurity. The theoretical normal volume found 388.1 leads to a molar weight of 57.77. If we assume the admixture to be ethane, its amount may be calculated from the molar weights of ethane (30.05) and butane (58.08): the amount of ethane would appear to be 1%.

The above result respecting the nature of the admixture finds confirmation in the boiling point of our butane. This point ($-1^{\circ}.0$) ⁴⁾ was derived from determinations of the vapour pressure in the neighbourhood of 0° :

temp.	press. (atm.)
12.0	1.6
0.00	1.049
0.00	1.046
-6.2	0.79

Owing to the presence of a more volatile admixture (ethane) the boiling point will be too low. In order to remove it to a certain extent the butane was cooled in solid carbon dioxide and vapour was pumped off. After this operation the vapour pressure at 0° was again measured; it was now 1.035 atm. The boiling point has therefore actually been raised: it now becomes -0.8° . In repeating the same operation a large portion of the vapour coming off was collected in the bulb of the mercury pump. The pressure above the small quantity of liquid left, appeared to have diminished to 1.027 atm.,

¹⁾ For these data we are indebted to Mr. G. Holst, whose results, which were worked out in the Leiden Laboratory, will shortly be published as a thesis at Zürich.

²⁾ Calculated from S. Young's data.

³⁾ Deduced from the above value of B .

⁴⁾ In Comm. 125 p. 4 by a clerical error the boiling point was given as -0.1° .

which means a further rise of the boiling point: the final value may be taken at -0.6°C .

A further confirmation of the presence of an admixture like ethane is afforded by the value of the critical temperature (150.8°). When for the various saturated hydrocarbons a graphical curve is drawn with the molar weights as abscissae and the corresponding critical temperatures as ordinates, the value found for butane seems to be a little too small. By representing the critical temperatures of ethane ($305^{\circ}.3$), pentane ($470^{\circ}.3$), hexane ($507^{\circ}.9$), heptane ($539^{\circ}.95$) and octane ($569^{\circ}.3$) as an arithmetical series of the fourth order, we find for propane $370^{\circ}.25$ instead of the experimental value $370^{\circ}.1$ and for butane $424^{\circ}.94$, i.e. $1^{\circ}.04$ higher than what was obtained by us. This result also points to a deviation of the critical temperature owing to the presence of a more volatile admixture.

Physics. — "*The viscosity of the vapour of normal butane*". By J. P. KUENEN and S. W. VISSER.

(Communicated in the meeting of September 27, 1913).

For the determination of the viscosity of butane vapour RANKINE's¹⁾ transpiration method was used; a method which is very simple and requires very little vapour, and in which the vapour comes into contact with glass and mercury only.

The apparatus consists of a long *O*-tube placed vertically and capable of being turned over on a horizontal axis. One arm of the *O* is capillary, the other one a wider tube. The vapour is forced through the capillary by a falling drop of mercury in the wide tube. When the drop has arrived at the bottom of the tube, the apparatus is simply turned upside down, and the drop now drives the gas through the capillary in the opposite direction. The time is measured between the moments at which the mercury passes two marks on the fall-tube. The whole tube is mounted in a glass jacket, where the temperature is kept constant.

In order to be able to work with a long capillary without making the apparatus unwieldy by its length, a capillary is used which is twice bent round: hereby it becomes almost three times as long as the wide tube.

¹⁾ A. O. RANKINE, Proc. Roy. Soc. London A 83, 265, 516; 1910.