

Reports

Temperature Regulation by the Inflorescence of Philodendron

Abstract. *The inflorescence of Philodendron selloum temporarily maintains a core temperature of 38° to 46°C, despite air temperatures ranging from 4° to 39°C, by means of a variable metabolic rate. The heat is produced primarily by small, sterile male flowers that are capable of consuming oxygen at rates approaching those of flying hummingbirds and sphinx moths.*

The inflorescences of several species of plants belonging to the arum lily family (Araceae) become much warmer than their surroundings during part of the 2- to 4-day flowering sequence (1). Typically, the inflorescence (spadix) warms rapidly, and then remains at its maximum temperature for 0.3 to 4.0 hours before cooling. Heating occurs at a specific time of the day and is apparently stimulated by an unidentified hormone (2) released in response to variations in light intensity (3). The heat, produced by the rapid oxidation of starch (4), results in the volatilization of chemicals that attract insect pollinators (5). The similarities between spadix temperature maintenance and endothermy in birds and mammals prompted us to investigate the thermal relations and energetics of these plant structures.

Continuous recording (6) of core temperatures (T_b) of the spadices of common garden philodendrons (*Philodendron selloum*) growing outdoors on the Los Angeles campus of the University of California revealed that the maximum temperatures of the spadices were maintained about 20°C higher than air temperatures (T_a). To examine the responses of spadices to a wider range of T_a than occurred outdoors, warming spadices were cut from the parent plant 1 to 2 hours before the peak T_b was due to be reached (about 19:30 P.S.T.) and placed in open 4-liter jars in a bacteriological incubator (Aminco); their T_b were monitored continuously at T_a ranging from 4° to 39°C (7). Most T_b were already about 35°C at the time the spadices were cut. In some, the green bract (spathe) partly enclosing the spadix was left intact.

To evaluate the effect of cutting inflorescences from the parent plant, the T_b of several spadices which had been severed from plants but left outside in situ were compared with T_b recorded from uncut spadices.

Maximum spadix temperatures were maintained within a relatively narrow range (means from 38.6° to 45.8°C), even when T_a was near freezing (Fig. 1). The least-squares regression line for these data has a small positive slope ($y = 0.179x + 38.2$; correlation coeffi-

cient $r = .77$), and the slope is significantly different (probability $P < .005$) from zero (8), an indication that T_b is partly dependent on T_a . Neither the removal of the spathes nor the cutting of the spadices from the parent plant had any detectable effect on T_b responses.

To determine the relationship between energy metabolism and T_b maintenance, we simultaneously measured rates of O_2 consumption and T_b at various T_a . We determined the amount of O_2 consumed by sealing the jars containing the spadices for 5 or 10 minutes and measuring the decrease in O_2 with a paramagnetic oxygen analyzer (Beckman model E2). Metabolic rates during peak temperature maintenance were inversely proportional to T_a (Fig. 1). At low T_a , the rates of O_2 consumption of spadices are comparable to those of resting hummingbirds (9) and small shrews (10).

To provide an independent check on O_2 consumption results, we measured the cooling rates of the same spadices used for metabolic rate measurements. After the spadices had been killed by freezing, they were heated to 50°C and then cooled under the same conditions obtaining during O_2 consumption measurements. Cooling rates in degrees Cel-

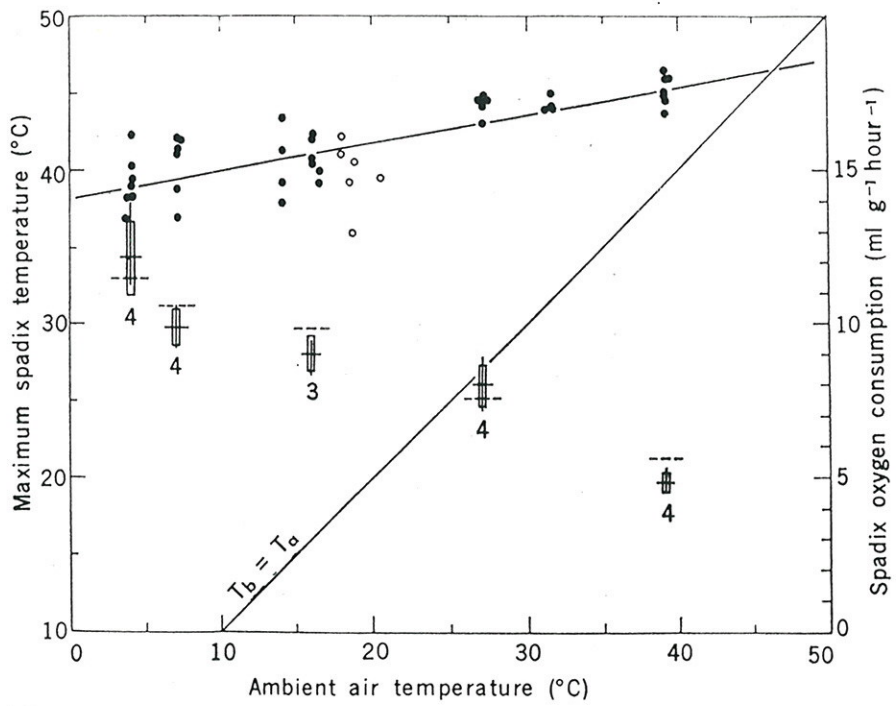
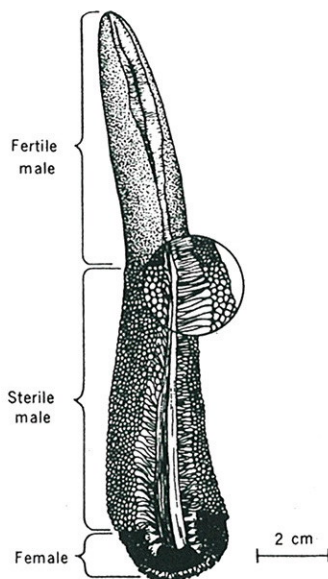


Fig. 1. Maximum core temperatures of philodendron inflorescences outdoors (○) and in incubators set at various temperatures (●). Solid horizontal lines indicate the mean spadix O_2 consumption rates; vertical lines show the ranges; rectangles are \pm standard deviations. Dashed horizontal lines indicate the mean metabolic rates predicted from the cooling rates of killed spadices. Numbers below the rectangles are sample sizes for O_2 consumption and cooling rate measurements.

Fig. 2. Structure of an inflorescence (spadix) of *Philodendron selloum*. This spadix was cut longitudinally to show the insertion and structure of the three types of flowers on the stalk (magnified in the circle). The spadix is contained within a large green bract (spathe) which opens at the onset of the flowering sequence.



sius per minute ranged from $1.54^\circ \pm 0.14^\circ$ (standard error) when $T_a = 4^\circ\text{C}$ to $0.77^\circ \pm 0.09^\circ$ when $T_a = 39^\circ\text{C}$. We used these rates to estimate the metabolic rates necessary to maintain T_b at a given value by using the equation (11)

$$M = K (dT/dt)$$

where M is the metabolic rate, K is the specific heat capacity [$0.595 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ for spadices, determined by the method of mixtures (12)], and dT/dt is the instantaneous rate of cooling when T_b of the cooling body equals T_b during temperature maintenance. The metabolic rates predicted from this equation are in good agreement with the measured rates (Fig. 1).

Thus philodendron inflorescences maintain constant, relatively high temperatures for brief periods of time by regulating their rate of oxidative metabolism. The ecological significance of this phenomenon is not clear; possibly the vaporization characteristics of the insect-attracting chemicals produced by philodendron are important in this regard. In another arum (*Sauromatum guttatum*), the volatilization rate of at least one chemical is increased twofold as a result of spadix heating (5).

In an effort to examine in further detail the control of respiration in philodendron, we measured the O_2 consumption rates of separate parts of the spadix. There are three flower types attached to the outside of the spadix stalk (Fig. 2). In a typical 125-g spadix female, flowers (weighing about 11 g when removed from stalk) occupy the base, sterile male flowers (about 36 g) occur in the middle section, and the distal end contains fertile male flowers (about 29 g). Preliminary measurements revealed that sterile male flowers possessed the highest weight-specific O_2 consumption rate, fertile male flowers consumed O_2 at about half that rate, whereas female flowers and stalk tissue consumed very little O_2 . To test the effects of temperature, we removed 2 to 4 g of sterile male flowers from the stalk and spread them on the bottom of 0.5-liter jars placed in incubators set at various temperatures. With the use

of this procedure any metabolic heat produced was rapidly dissipated, and the temperature of the flowers remained near T_a .

Under these conditions, rates of O_2 consumption increased with temperature to a peak at 37°C and then decreased at higher temperatures (Fig. 3), in the same manner as in isolated mammalian and avian tissues and most isolated enzyme preparations. The highest metabolic rate, when $T_a = 37^\circ\text{C}$, was almost 30 ml of O_2 per gram per hour; this approaches the metabolic rate of 40 to 50 ml of O_2 per gram per hour measured in hovering hummingbirds (9) and flying sphinx moths (13).

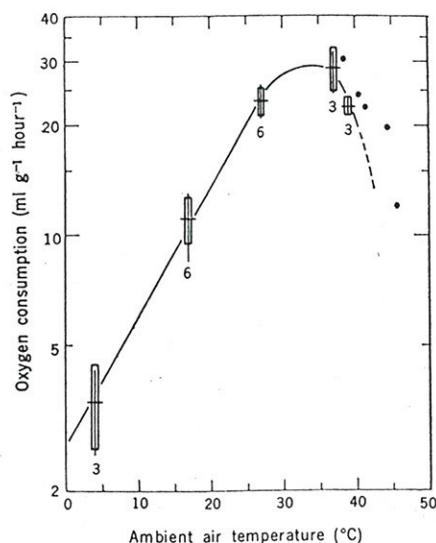


Fig. 3. Relationship between the metabolic rate of sterile male flowers removed from philodendron spadices and temperature ($T_b \cong T_a$). Solid circles represent values calculated from the O_2 consumption rates of intact spadices (13). Other symbols are as in Fig. 1.

We constructed a model, based on these results, that can account for the ability of spadices to regulate maximum T_b . The metabolic rates of isolated flowers drop rapidly when T_a is increased from 37° to 39°C (Fig. 3). If this trend continued to 45°C , the result would be a large change in metabolic rate over a narrow temperature range. Thus, if a spadix maintaining T_b at a given T_a somehow became warmer, O_2 consumption and metabolic heat production would decrease, causing the spadix to cool and return to the steady-state condition. The reverse would occur in a cooling spadix. The temperatures at which spadices reach the steady state should increase with T_a for the following reasons: (i) because the rate of heat loss is proportional to the temperature difference ($T_b - T_a$); (ii) because temperature maintenance requires that heat loss equals heat production; and (iii) because the model predicts that, when T_b is above 37°C , rates of heat production decrease with increasing T_b . This prediction agrees with the observed correlation between T_b and T_a (Fig. 1).

Unfortunately, the flowering season ended before we could test this model by measuring O_2 consumption of isolated flowers at temperatures above 39°C . However, we calculated estimates of these values from mean O_2 consumption rates of intact spadices (Fig. 1) by correcting for the fraction of total spadix weight that consists of sterile and fertile male flowers, and the relative metabolic rates of both flower types (14). When these values are plotted against the corresponding mean T_b for each group of spadices (Fig. 3), a steep inverse relationship results, thus indirectly supporting the basic assumption of the model.

It appears that the lowest T_a at which philodendron spadices can maintain a high T_b is near 4°C . In fact, two small spadices did not remain warm when placed in the 4°C incubator but rapidly cooled to 4°C . Apparently their larger ratio of surface to mass occasioned heat loss that exceeded the maximum heat production, thus providing for the cooling of metabolizing tissues and the concurrent disruption of the balance between body temperature, energy metabolism, and heat loss.

KENNETH A. NAGY
DANIEL K. ODELL
ROGER S. SEYMOUR*

Department of Biology,
University of California,
Los Angeles 90024

References and Notes

1. A. W. H. van Herk, *Rec. Trav. Bot. Neer.* 34, 69 (1937); L. van der Pijl, *ibid.*, p. 157; B. J. D. Meeuse, *Sci. Amer.* 215, 80 (July 1966); B. H. Brattstrom, *Bull. South. Calif. Acad. Sci.* 71, 54 (1972).
 2. R. G. Buggeln and B. J. D. Meeuse, *Can. J. Bot.* 49, 1373 (1971).
 3. B. J. D. Meeuse and R. G. Buggeln, *Acta Bot. Neer.* 18, 159 (1969); R. G. Buggeln, B. J. D. Meeuse, J. R. Klima, *Can. J. Bot.* 49, 1025 (1971).
 4. W. O. James and H. Beevers, *New Phytol.* 49, 353 (1950); D. P. Hackett, *J. Exp. Bot.* 8, 157 (1957); E. W. Simon, *ibid.* 10, 125 (1959); D. S. Bendall and W. D. Bonner, Jr., *Plant Physiol.* 47, 236 (1971).
 5. B. N. Smith and B. J. D. Meeuse, *Plant Physiol.* 41, 343 (1966).
 6. All temperatures were recorded with copper-constantan thermocouples connected to a multipoint strip-chart recorder (Honeywell Electronic 16).
 7. A fan in the incubator circulated the air and kept T_a within $\pm 0.5^\circ\text{C}$.
 8. Using the *t*-test from W. J. Dixon and F. J. Massey, Jr., *Introduction to Statistical Anal-*

ysis (McGraw-Hill, New York, ed. 3, 1969), p. 197.
 9. R. C. Lasiewski, *Physiol. Zool.* 36, 122 (1963).
 10. O. P. Pearson, *Science* 108, 44 (1948).
 11. Derived from equations and assumptions presented by G. A. Bartholomew and V. A. Tucker, *Physiol. Zool.* 36, 199 (1963).
 12. R. C. Weast and S. M. Selby, Eds., *Handbook of Chemistry and Physics* (Chemical Rubber Company, Cleveland, ed. 48, 1967), p. F-87.
 13. B. Heinrich, *J. Exp. Biol.* 54, 141 (1971).
 14. The equation used was: spadix O_2 consumption (in milliliters of O_2 per gram per hour) = (0.29 g of sterile male flowers per gram of spadix) multiplied by (X) + (0.23 g of fertile male flowers per gram of spadix) multiplied by (X/2), where X is the O_2 consumption rate of sterile male flowers and X/2 is the metabolic rate of fertile male flowers.
 15. We thank K. Pogany for preparing the illustration in Fig. 2. This study was supported in part by NSF grant GB-32947X to Dr. G. A. Bartholomew.
 * Present address: Department of Zoology, Monash University, Clayton, Victoria 3168, Australia.
 2 October 1972

hazard to human health, it should be based not on the composition of the wrapper but rather on the physicochemical properties of the smoke and its resulting "inhalability." In this study we attempted to establish the specific physicochemical differences between the smoke of cigarettes, cigars, and the new, popular little cigars. It is hoped that this information will contribute to the establishment of new ways of distinguishing between cigarettes, cigars, and little cigars which are more relevant to human health.

Cigarettes without filter tips (85 mm) were obtained from the University of Kentucky (3); little cigars A (85 mm), from the open market in Boston, Massachusetts (December 1971); filter cigarettes (85 mm), little cigars B (85 mm), small cigars C (95 mm), and cigars D (112 mm), from the open market in New York City (December 1971–January 1972). The filter cigarettes, little cigars B, small cigars C, and cigars D chosen were the largest-selling brands in their respective categories (4).

The tobacco products (5) were humidified in a chamber maintained at a relative humidity of 60 percent and 22°C and subsequently smoked under standard conditions as established for cigarettes (6). Standard smoking conditions are as follows: a single puff of 2 seconds duration once a minute; a puff volume of 35 ml; a butt length of 23 mm except for the filter cigarette and little cigar A which have butt lengths of 27 mm. Subsequently, we determined the burning rate as an indicator of combustibility (6); total particulate matter (TPM) and nicotine as

Smoke of Cigarettes and Little Cigars: An Analytical Comparison

Abstract. *Chemical data are presented from a comparison study of the smoke of cigarettes and little cigars. The tobacco products and their mainstream smokes were analyzed for a number of toxic constituents in an effort to define "smoke inhalability." This issue has particular public health importance because the difference in the inhalability of cigar and cigarette smoke is generally assumed to account for the differences in the health risk to the individual smoker.*

Epidemiological studies have demonstrated that the chance of developing lung cancer is greater for cigarette smokers than for cigar smokers; however, both types of smokers face the same risk of developing cancer of the oral cavity. The difference in the rate at which cigar and cigarette smokers develop lung cancer is related to known differences in inhalation practices which are, in turn, dependent on the physicochemical properties of the different smokes (1).

At present, in the United States, the distinction between a cigar and a cigarette is based on the 1961 Internal Revenue Service definition, made for tax purposes, which defines a cigar as "any roll of tobacco wrapped in leaf tobacco or in any substance containing tobacco" and a cigarette as "any roll of tobacco wrapped in paper or any substance not containing tobacco" (2).

It is obvious that, if the distinction between cigars and cigarettes is to be meaningful in terms of the potential

Table 1. Analysis of cigarettes and little cigars and some of their smoke constituents.

Parameter	Nonfilter cigarette	Filter cigarette	Little cigar A	Little cigar B	Small cigar C
Filter length (mm)		21	21	18	15
Weight (mg)	1100	1010	956	1078	1522
Weight without filter (mg)		845	775	934	1355
Reducing sugars (% of tobacco weight)	9.3	7.9	1.5	2.9	2.7
Draw resistance* (mm)	6.6	13.4	13.2	13.0	8.9
Burning rate (mg of tobacco per minute)	51.3	61.7	72.7	61.0	90.1
Average number of puffs	11.0	10.0	7.7	9.8	11.6
Nicotine (mg)	2.65	1.4	0.6	1.8	3.1
TPM† (mg)	36.1	20.3	17.4	31.8	40.6
Average pH, 3rd puff	6.19	6.15	6.44	6.55	6.55
Average pH, 5th puff	6.14	6.12	6.57	6.46	6.59
Average pH, 7th puff	6.09	6.01	7.03	6.51	6.56
Average pH, 9th puff	6.02	5.83		6.98	6.59
Average pH, last puff‡	5.96 (11)	5.76 (10)	7.73 (8)	7.25 (10)	7.11 (11)

* For an air flow of 17.5 ml/sec. † Federal Trade Commission value for TPM = TPM wet minus water and minus nicotine. ‡ The number in parentheses is the number of the last puff. Average pH values of cigar D: 6.47 (3); 6.27 (8); 6.39 (13); 6.41 (18); 6.81 (23); 7.22 (28); 7.53 (33); 7.78 (38); 7.96 (43); [average number of puffs: (45)].

Table 2. Selected compounds in mainstream smoke.

Smoke component	Concentration	Nonfilter cigarette	Filter cigarette	Little cigar A	Little cigar B	Small cigar C
Carbon monoxide	Vol. %	4.6	4.5	5.3	11.1	7.7
Carbon dioxide	Vol. %	9.4	9.6	8.5	13.2	12.7
Hydrogen cyanide	µg/cig.	536	361	381	697	1029
Acetaldehyde	µg/cig.	770	774	630	1238	1150
Acrolein	µg/cig.	105	71	41	54	66
Pyridine	µg/cig.	24.8	11.0	24.2	35.8	29.5
α-Picoline	µg/cig.	13.1	4.5	9.4	13.6	11.5
β-Picoline	µg/cig.	23.0	5.6	12.6	20.3	19.0
γ-Picoline	µg/cig.	6.8	2.0	3.5	6.4	5.9
Lutidines*	µg/cig.	15.1	4.2	8.3	9.2	14.4
Total pyridines	µg/cig.†	82.8	27.3	58.0	85.3	80.3
Phenol	µg/cig.	124.2	33.0	35.1	63.4	94.1
o-Cresol	µg/cig.	24.0	6.8	4.0	10.0	19.5
m- + p-Cresol	µg/cig.	75.4	22.2	16.9	37.8	67.1
2,4- + 2,5-Dimethylphenol	µg/cig.	9.4	4.6	1.0	3.7	6.1
m- + p-Ethylphenol	µg/cig.	22.1	9.2	6.5	17.6	27.0
Benz[a]anthracene	ng/cig.	74	31	34	25	39
Benzo[a]pyrene	ng/cig.	47	20	18	22	30

* Sum of values for 2,6-, 2,4-, and 3,5-lutidines which were determined individually by gas chromatography. † Value for cigar D, 536.1 µg.

an indicator of toxicity (7-9); the total smoke pH as an indicator of the degree of nicotine toxicity (10); carbon monoxide, carbon dioxide, and hydrogen cyanide as an indicator of the toxicity of the gas phase (11, 12); acetaldehyde and acrolein as an indicator of the cilia toxicity (7); pyridines as an indicator of the toxic and taste-affecting volatile bases (11); the phenols as an indicator of volatile tumor promoters (13); and benz[a]anthracene and benzo[a]pyrene as examples of tumor initiators (14). We also determined the total concentrations of reducing sugars in the various tobacco products. We tested cigar D only for pH and pyridine content. The results summarized in Tables 1 through 3 are average values from three tests each.

The concentration of total reducing sugars in the tobacco of little cigars is significantly lower than that in the tobacco of blended cigarettes (Table 1). This result was expected since cigars are reported to contain only air-cured

and fermented tobaccos. These tobaccos have significantly lower concentrations of reducing sugars than flue-cured or sun-cured tobaccos. These data need further investigations since the low concentration of total reducing sugars in these tobacco types is related to the relatively low concentration of acids in the tobacco and thereby to the increasing pH value of the total smoke of these tobaccos. At hydrogen ion concentrations below 10^{-6} ($> pH 6$), tobacco contains increasing amounts of unprotonated nicotine (and other pyridines), the most toxic form of nicotine in tobacco smoke.

The burning rate of little cigars with filters is relatively rapid, resulting in a low number of puffs for the amount of tobacco in these products (Table 1). The "tar" (TPM) and nicotine concentrations in the mainstream smoke of little cigar A are lower than expected as compared to other small cigars. This result is at least partially attributable to the types of tobacco selected and to the incorporation of puffed tobacco

and reconstituted tobacco sheets into the tobacco blend (revealed when samples were examined under the microscope) (15).

The pH values for the total smoke of little cigar A show that the smoke of the last two puffs is basic ($pH > 7.0$; Table 1). Indeed, our results indicate that as much as 30 to 40 percent of the smoke of regular cigars is basic in nature. Since only the last two puffs of little cigar A evolve smoke of a basic nature and since the nicotine concentration of the smoke is quite low, one may expect that the smoker of little cigar A is more likely to inhale the smoke than the smoker of other little cigars. The smoker of standard cigars and most little cigars is, however, unlikely to inhale the smoke since the higher nicotine concentration of the cigar smoke, coupled with a high pH, makes the inhalation of cigar smoke unpleasant.

The smoke of little cigar A has carbon monoxide and carbon dioxide concentrations comparable to those of cigarette smoke [Table 2; see also (7)], whereas the carbon monoxide and carbon dioxide concentrations for little cigar B and small cigar C are significantly higher. The low concentrations of hydrogen cyanide, acetaldehyde, and acrolein in little cigar A also indicate that this tobacco product is unusually mild (Table 2). The volatile pyridines are primarily pyrosynthesized from tobacco alkaloids. They are assumed to give the smoke its undesirable taste and to contribute to the strength of the smoke flavor of cigars. Table 2 shows that the mainstream smoke of little and small cigars with filter tips have considerably higher concentrations of pyridines than filter cigarettes but significantly lower concentrations of volatile pyridines than cigars. This finding supports the concept that the taste of the smoke of the little cigar is less harsh than that of cigars. The concentration of volatile phenols is also very low for little cigar A. This results not only from the tobacco blend but also from the

Table 3. Some selected toxic agents in the smoke of a single puff (total smoke divided by the number of puffs needed to reach the standard butt length).

Sample	TPM* (mg)	Nicotine (mg)	pH (last puff)	Carbon monoxide (volume %)	Carbon dioxide (volume %)	Hydrogen cyanide (µg)	Total pyridines (µg)
Nonfilter cigarette	3.28	0.259	5.96	4.6	9.4	48.7	7.6
Filter cigarette	2.03	.140	5.76	4.5	9.6	36.1	2.7
Little cigar A	2.25	.078	7.73	5.3	8.5	49.5	7.6
Little cigar B	3.24	.183	7.25	11.1	13.2	71.1	8.7
Small cigar C	3.50	.267	7.11	7.7	12.7	88.7	6.9

* Federal Trade Commission value for TPM = TPM wet minus water and minus nicotine.

selective removal of these agents by the cellulose acetate filter which contains plasticizers [Table 2; (6)]. The ratio of *m*- and *p*-ethylphenol to 2,4- and 2,5-dimethylphenol is significantly greater in little cigar smoke than in cigarette smoke. At present, we do not know the importance of this observation. The concentration of benz[a]anthracene and benzo[a]pyrene in the smoke of little cigar tobacco is relatively low (Table 2). This result was expected for tobacco products which are made up largely of cigar type or air-cured tobacco and reconstituted tobacco sheets (7, 17).

Our preliminary data indicate that, on a per puff basis (Table 3), the reduced levels of "tar," nicotine, and carbon monoxide may permit the tobacco user to inhale the smoke of some little cigars even though it is otherwise just as toxic as the "uninhaled" smoke of conventional cigars.

DIETRICH HOFFMANN
ERNEST L. WYNDER

Health Research Institute,
American Health Foundation,
New York 10021

References and Notes

1. E. L. Wynder and E. A. Graham, *J. Amer. Med. Ass.* **143**, 329 (1950); M. L. Levin, H. Goldstein, P. R. Gerhardt, *ibid.*, p. 336; Royal College of Physicians, London, *Smoking and Health* (Pitman Medical, London, 1962); U.S. Public Health Rep. No. 1103 (1964); U.S. Public Health Rep. No. 1696 (1967); U.S. Public Health Rep. 1696-Suppl. (1968); U.S. Public Health Rep. 1696-2 (1969); Royal College of Physicians, London, *Smoking and Health Now* (Pitman Medical, London, 1971); U.S. Dep. Health Educ. Welfare Publ. No. (Health Serv. Mental Health Adm.) 71-7513 (1971); U.S. Dep. Health Educ. Welfare (Health Serv. Mental Health Adm.) Publ. No. 72-1516 (1972).
2. U.S. Department of Treasury, Internal Revenue Service, "Code of Federal Regulations 26," part 270, "Manufacture of Cigars and Cigarettes" (1972), p. 759.
3. The Kentucky standard cigarettes are manufactured for research purposes only. Their "tar" yield is rather high as compared to commercial U.S. cigarettes of the same length and without filter tips.
4. J. C. Maxwell, Jr., *Tob. Rep.* **98** (No. 10), 20 (1971).
5. U.S. Dep. Agr. Tech. Bull. 1225 (1969), p. 117, method 34.
6. D. Hoffmann and E. L. Wynder, *Cancer Res.* **27**, 172 (1967).
7. E. L. Wynder and D. Hoffmann, *Tabacco and Tobacco Smoke* (Academic Press, New York, 1968).
8. H. C. Pillsbury, C. C. Bright, K. J. O'Connor, F. W. Irish, *J. Ass. Offic. Agr. Chem.* **52**, 458 (1969) (official method of the Federal Trade Commission).
9. F. J. Schultz and A. W. Spears, *Tob. Sci.* **10**, 75 (1966).
10. A. J. Sensabaugh, Jr., and R. H. Cundiff, *Tob. Sci.* **11**, 25 (1967).
11. D. Hoffman, K. Brunnemann, G. Rathkamp, unpublished data.
12. A. Artho and R. Koch, *Beitr. Tabakforsch.* **5**, 58 (1969).
13. D. Hoffmann and E. L. Wynder, *ibid.* **1**, 101 (1961) (¹⁴C]phenol was the internal standard).
14. G. Rathkamp and D. Hoffmann, *ibid.* **5**, 302 (1970).
15. In general, air-cured tobaccos, freeze-dried (puffed) tobaccos, and reconstituted tobaccos deliver less "tar" than flue-cured tobaccos.

The freeze-drying process results in a tobacco leaf with modified structural properties and increased specific volume. Reconstituted tobacco sheets are made of a mixture of tobacco fines, tobacco midribs, and opened tobacco stems. To this mixture certain cellulose derivatives are sometimes added.

16. D. Hoffmann and E. L. Wynder, *J. Nat. Cancer Inst.* **30**, 67 (1963).

17. ———, *Nat. Cancer Inst. Monogr.* **28**, 151 (1968).

18. Supported in part by American Cancer Society grant BC 56P and by National Cancer Institute grant NIH-NCI-70-2087. This is report number XVIII in a series of papers entitled "Chemical Studies on Tobacco Smoke" by D.H. and E.L.W.

9 August 1972; revised 26 September 1972

Gravitational Effects on Concentrations and Partial Pressures in Solutions: A Thermodynamic Analysis

Abstract. Thermodynamic analysis establishes the equilibrium relationships between the concentrations and partial pressures of the components of liquid and gaseous solutions in the presence of a gravitational field. The conditions of equilibrium between a column of gas and gas-saturated water and the conditions of equilibrium governing a model of the distribution of radioactive heat sources in surface rocks are deduced from the theory.

In a recent report, Fenn (1) discussed a series of experiments by Enns *et al.* (2), in which the equilibrium through a semipermeable membrane between a gas column and a gas-saturated liquid was studied as a function of depth. In another report, Turcotte and Oxburgh (3) suggested that the exponential dependence of the concentration of radioactive heat sources on depth observed in near-surface rocks by Lachenbruch (4) could be explained simply in terms of the Boltzmann factor of equilibrium statistical mechanics. I develop here the equilibrium criteria for solutions in the presence of a gravitational field so that both sets of phenomena are described.

The logical structure of equilibrium thermodynamics in the presence of gravitational fields is based on the addition of a term ψdm to the usual Gibbs expression for the differential of the internal energy. Here, ψ is the gravitational potential and dm the change in mass in the region considered. The inclusion of this term assures proper bookkeeping of the total energy when mass dm is moved from one region to another, with the resulting energy change, $(\psi_2 - \psi_1)dm$, in accordance with the definition of gravitational potential. Since dm for a mixture is the sum of terms $M_i dn_i$ over all components i , where M_i is the molecular weight and n_i is the number of moles of i , the Gibbs equation with gravity is identical to the Gibbs equation without gravity, except that with gravity $\mu_i + M_i \psi$ replaces the chemical potential, μ_i . It is a straightforward consequence of the second law of thermodynamics that at equilibrium in the absence of a gravitational field μ_i is the same in all regions of the system which

can interchange components i (5, p. 93). The identical proof with gravity therefore shows

$$\mu_i + M_i \psi = \text{constant} \quad (1)$$

to be the generalized equilibrium criterion, along with the usual constancy of the temperature, T .

From Eq. 1 the criterion for hydrodynamic equilibrium follows if we insert the derivative of Eq. 1

$$d\mu_i = -M_i d\psi$$

into the Gibbs-Duhem equation

$$V dp - \sum_i n_i d\mu_i = 0$$

for a small region V centered on the point of interest. Division of the result by V yields

$$dp + \rho d\psi = 0 \quad (2)$$

(where p is the pressure and ρ is the density of the medium at any depth), the criterion for lack of bulk fluid flow. This criterion can be integrated for gases if we substitute

$$p = m/V = pM(y)/z(y)RT$$

where z is the compressibility factor for the gas at the point y , M is the weight of an Avogadro number of molecules taken about the point y , R is the gas constant, and T is the absolute temperature. If $\psi = -gy$, where y is the depth, g is the magnitude of the gravitational field, and in the ideal gas approximation where $z = 1$, the barometric formula results:

$$p_{\text{gas}}(y) = p_{\text{gas}}(0) \exp(Mgy/RT) \quad (3)$$

where M is the average molecular weight of the gas between 0 and y . The criterion, Eq. 2, may also be integrated for liquids if one knows how ρ changes