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Rate of evaporation of n-alcohols from a hot surface: Nukiyama and Leidenfrost temperatures

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Abstract The Nukiyama and Leidenfrost temperatures of the range of n-alcohols from methanol (C_1) to tetradecanol (C_{14}) have been investigated, and their relationships to the standard boiling points determined. The Nukiyama temperatures prove to be some 46°C above the latter, with a further rise of only $15\text{--}18^\circ$ sufficing to put an alcohol into the slowly evaporating Leidenfrost regime.

1. Introduction

A previous paper (Mills and Fry 1982) explains the difference between nucleated and non-nucleated boiling of liquids upon a hot surface, defines the Nukiyama and Leidenfrost temperatures, and gives quantitative results for the homologous series of normal hydrocarbons from pentane to hexadecane. In that paper it was suggested that investigation might well be extended to the alcohols, for although the film boiling phenomenon was first observed with ethanol by Boerhaave (1732) subsequent work has been almost entirely confined to water. Although employing comparatively simple apparatus, careful technique would therefore produce useful original data relevant to industrially important materials. This research was chosen by Noëlle F Sharrock for her third-year BSc project, working with A A Mills of the academic staff.

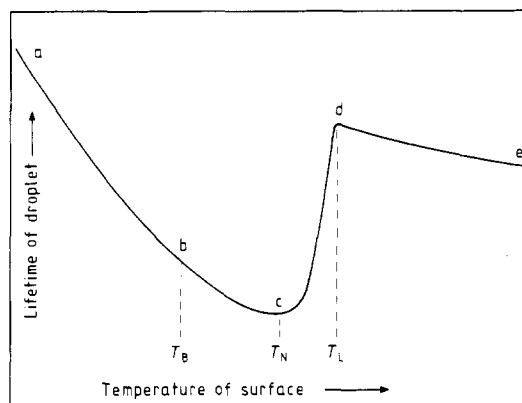
2. Nukiyama and Leidenfrost temperatures

The lifetime of a droplet of a volatile liquid placed upon a hot surface is not a simple function of temperature, but according to Tamura and Tanasawa (1959) follows the generalised curve shown in figure 1. The liquid begins to boil at nucleated sites in the interface at a temperature T_B , and as the temperature of the hot surface is increased so the number of nucleated sites and the rate of evaporation increase, whilst the drop lifetime diminishes. However, this 'expected' behaviour does not continue indefinitely, for

Zusammenfassung Die Nukiyama and Leidenfrost Temperaturen der Reihe der n-Alkohole von Methanol (C_1) zu Tetradekanol (C_{14}) wurden untersucht und ihre Beziehung zu den Standard Siedepunkten bestimmt. Die Nukiyama Temperaturen liegen etwa 46°C oberhalb der letzteren, wobei eine weitere Erhöhung um $15\text{--}18^\circ\text{C}$ genügt, um einen Alkohol in das Leidenfrost-Gebiet der langsamem Verdampfung zu überführen.

above a certain temperature the droplet becomes supported by a thin film of its own vapour and, moving freely over the hot surface, takes a remarkably long time to evaporate completely. This move into a non-nucleated film boiling regime begins at point c on the curve, associated with a minimum lifetime and maximum rate of evaporation: we have called the corresponding temperature the Nukiyama temperature

Figure 1 Generalised curve of the lifetime of an evaporating droplet plotted against the temperature of the supporting surface.



T_N (Nukiyama 1934). At point d the supporting vapour film is fully developed, the droplet is completely separated from the hot surface, and the liquid displays a minimum rate of evaporation for a temperature exceeding its normal boiling point. The associated temperature is conventionally known as the Leidenfrost temperature T_L . (A more detailed discussion is given by Mills and Fry (1982).) The Nukiyama and Leidenfrost temperatures are not fundamental properties of the liquid being heated, being obviously dependent on pressure and, to a lesser extent, the composition and finish of the hot surface.

3. Previous work

A literature search disclosed some early data for methanol and ethanol.

	Nukiyama temperature T_N (°C)	
	Methanol	Ethanol
Mosciki and Broder (1926)	94	103
Blaszowska-Zakrzewska (1930)	—	110–115
Sauer <i>et al</i> (1938)	108–120	107–124

Boutigny (1843) obtained 134 °C for the Leidenfrost temperature T_L of ethanol.

4. Apparatus and technique

The apparatus used for the previous work on hydrocarbons was employed. It consisted of a 25 mm diameter copper disc 3 mm thick, in one face of which was turned a smooth hemispherical depression of 50 mm radius of curvature. This disc was heavily plated with gold and then polished, providing a smooth, inert metal surface with a concavity serving to retain the mobile Leidenfrost droplets. This gilded dish was supported beneath a binocular microscope upon an electrically heated silver block forming the working section of a Linkam TH 600 mineralogical heating stage. It was carefully shielded from draughts. Input power was controlled by a proportional feedback thermostat, and any preset temperature could be measured and held constant to ± 0.2 °C. Calibration was carried out with standard substances of known melting point, and with an independent thermocouple.

Laboratory grade alcohols of the normal homologous series from C_1 (methanol) to C_{14} (tetradecanol) were obtained. Purity was always better than 97%. Each was freshly distilled before use, observing the boiling point T_B of the collected middle fraction. 5 μ l droplets of the alcohol under test were gently dispensed into the heated concave depression of the gilded dish with a preset calibrated micropipette

(‘Finnpipette’). These small volumes did not cool the hot-plate appreciably, so the measurements were made under essentially isothermal conditions. Lifetimes were determined with a stopwatch, beginning when a drop left the pipette. Observation through the microscope facilitated an accurate endpoint. Five drops were timed at each temperature, cleaning the surface between each determination with a lens tissue moistened with redistilled acetone.

5. Results and discussion

The drop lifetime curve for n-pentanol is reproduced in figure 2, and is typical of the results obtained. The change of slope following soon after T_B , and the slight convexity preceding the minimum at T_N , which were first noted by Mills and Fry (1982) for hydrocarbons, are again apparent with the alcohols. In addition, an oscillating behaviour above T_L becomes obvious. This was not remarked upon by the above authors, but can be distinguished (at a low amplitude) in their curves. We therefore believe that figure 2 more nearly represents in its details the true drop lifetime curve of liquids on a hot surface.

The values of T_B , T_N and T_L obtained for the homologous series of normal alcohols are shown in table 1. The figures given for the likely errors are

Figure 2 Drop lifetime curve for n-pentanol.

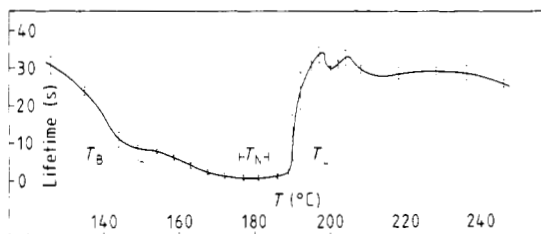


Table 1 The boiling point, Nukiyama and Leidenfrost temperatures (in °C) for the n-alcohols at atmospheric pressure.

	T_B ($\pm 1^\circ$)	T_N	T_L
Methanol	66	111 \pm 3.5	126 \pm 3
Ethanol	79	126 \pm 4	140 \pm 3
Propanol	98	145 \pm 3.5	160 \pm 3.5
Butanol	120	165 \pm 3.5	172 \pm 3.5
Pentanol	138	180 \pm 4	198 \pm 3
Hexanol	158	198 \pm 4	220 \pm 4
Heptanol	176	220 \pm 6	244 \pm 4
Octanol	194	236 \pm 4	254 \pm 4
Nonanol	212	256 \pm 4	273 \pm 4
Decanol	228	272 \pm 4	289 \pm 3
Undecanol	244	291 \pm 4	324 \pm 7
Dodecanol	260	299 \pm 7	324 \pm 7
Tridecanol	274	324 \pm 7	343 \pm 7
Tetradecanol	290	343 \pm 7	365 \pm 7

usually equivalent to $\pm 2-3\%$. Our values for T_N of methanol and ethanol correspond most nearly with those found by Sauer *et al* (1938).

Figure 3 shows plots of T_N and T_L against T_B . The graphs are linear within the experimental errors, and

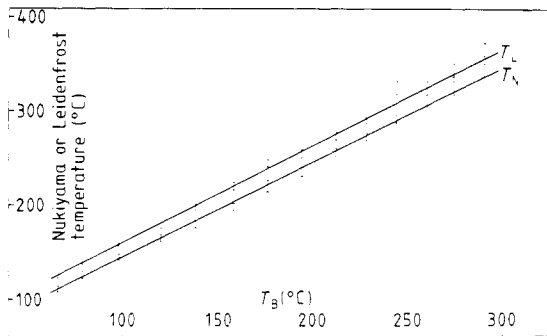
may be summarised by the relationships:

$$T_N = (1.01T_B + 44)^\circ\text{C}$$

$$T_L = (1.02T_B + 59)^\circ\text{C}.$$

In general, maximum rates of evaporation are achieved on hot surfaces maintained at $46 \pm 1^\circ\text{C}$ above the standard boiling point, with a further rise of only $15-18^\circ$ sufficing to put an alcohol into the slowly evaporating Leidenfrost regime.

Figure 3 Nukiyama and Leidenfrost temperatures of the n-alcohols plotted against their corresponding boiling points at atmospheric pressure.



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