Rate of evaporation of hydrocarbons from a hot surface: Nukiyama and Leidenfrost temperatures

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Abstract The Nukiyama and Leidenfrost temperatures of the range of n-alkanes from pentane to hexadecane have been investigated, and their relationships to the standard boiling points determined. The Nukiyama temperatures prove to be only some 40 °C above the latter, showing that maximum evaporation rates are produced by contact with surfaces not nearly so hot as might intuitively be expected. A temperature increase of only some 20–30 °C beyond this point is sufficient to put the hydrocarbon into the slowly-evaporating Leidenfrost regime.

Zusammenfassung Die Nukiyama und Leidenfrost Temperaturen für die n-Alkane zwischen Pentan und Hexadekan werden in ihrem Zusammenhang mit den Standardsiedepunkten bestimmt. Die Nukiyama Temperaturen liegen dabei nur etwa 40 °C oberhalb des Siedepunktes, was zeigt, daß die maximale Verdampfungsrate sich durch Kontake mit Oberflächen ergibt, die nicht annähernd so heiß sind, wie man dies intuitiv erwartet. Eine Temperaturerhöhung um etwa 20–30 °C über diesen Punkt hinaus reicht aus, um Hydrocarbone in den langsam verdampfenden Leidenfrost Bereich zu bringen.

1. Introduction

Most British university science departments now require some form of project as part of the assessment for a first degree. This period can frequently be profitably employed to allow students to become acquainted with phenomena that time does not allow to be included in lectures, and to discover for themselves that many topics are not nearly so thoroughly worked-over and understood as is commonly supposed. It is particularly satisfying if they can then reduce some of these gaps in our knowledge. An example is the evaporation of liquids other than water in the non-nucleated regime. An investigation of the behaviour of a homologous series of n-alkanes was chosen by J D Fry as his third-year project, working with A A Mills of the academic staff.

2. Nukiyama and Leidenfrost temperatures

Drops of a volatile liquid placed upon a hot surface will, of course, evaporate. However, according to Tamura and Tanasawa (1959) the lifetime of a droplet is not a simple function of temperature, but instead follows the generalised curve shown in figure 1.
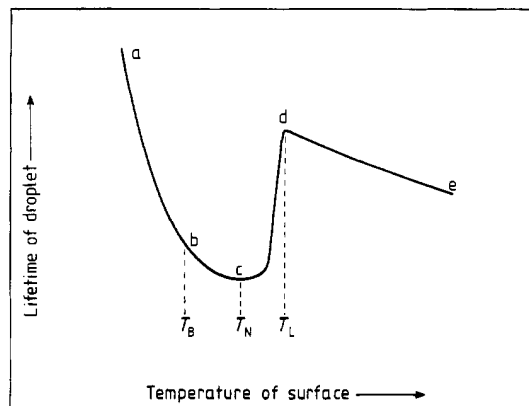

Figure 1 Generalised curve of the lifetime of an evaporating droplet versus temperature of the supporting surface.

When the temperature of the surface is below that corresponding to the normal boiling point of the liquid at the ambient pressure, the droplet either wets the surface and spreads out or, more commonly, assumes a plano-convex shape. It evaporates slowly and quietly along section a–b of figure 1.

At the boiling point T_B tiny vapour bubbles begin to appear at nucleated sites in the liquid/solid interface. The number of these sites, and consequently the rate of evaporation, increases with temperature along section b–c until, by the time c is reached, the lens-shaped droplet has been replaced by a violently boiling irregular mass. The rapid vaporisation occurring at a multitude of nucleated sites produces a hissing sound.

However, a comparatively small increase, to point d, in the temperature of the heated surface exerts a profound effect. The liquid gathers itself into flattened globules which, supported by a cushion of their own vapour, glide above the hot surface. This move into a non-nucleated, film-boiling regime is accompanied by a dramatic fall in the rate of evaporation, and constitutes the well-known Leidenfrost effect (Wares 1966, Bell 1967, Curzon 1978).

It will be seen that the *maximum* rate of evaporation (minimum lifetime; point c) is associated with a temperature which we propose to call the Nukiyama temperature T_N after its discoverer (Nukiyama 1934). This appears to us to be preferable to the rather ambiguous term 'crisis boiling point', especially as that temperature (above the normal boiling point) corresponding to a *minimum* rate of evaporation (point d) is already conventionally known as the Leidenfrost temperature T_L. The transitional section (c–d) of the curve is sometimes unstable and hard to define experimentally, but above T_L the levitated spheroids can be remarkably stable and reproducible along curve d–e. A very large temperature increase (typically some hundreds of degrees) is necessary before the overall rate of evaporation again approaches that observed at the Nukiyama temperature. Similar considerations apply to spillages of liquefied petroleum gases and cryogenic fluids boiling below ambient temperatures.

Nukiyama's observations on the related changes in heat flux from a hot wire or tube entirely submerged in a boiling liquid were confirmed and extended by subsequent workers, as detailed by Drew and Mueller (1937) and McAdams (1954). In more recent years considerable progress has been made in the understanding and theoretical prediction of the Leidenfrost phenomenon (Gottfried *et al* 1966, Baumeister and Simon 1973, Michiyoshi and Makino (1978). However, the Nukiyama temperatures of liquids other than water have received very little attention. This is surprising in view of the fact that evaporation of organic liquids (and especially petroleum hydrocarbons) is such an important process in modern technology. We have therefore examined the range of straight-chain alkanes from pentane to hexadecane.

3. Apparatus and technique

A shallow spherical depression of 50 mm radius of curvature was turned in a 25 mm diameter copper disc 3 mm thick, and smoothed with successively finer grades of diamond paste. A heavy coating (about 10 μm) of pure gold was then electroplated upon the copper, and the resulting surface highly polished. This produced a smooth, inert metal surface unaffected by the temperatures and materials used in the experimental runs. 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.

The purity of the hydrocarbons employed was better than 99%, and they were freshly distilled before use, observing the boiling point T_B of the collected middle fraction. Drops of the liquid under test were gently dispensed into the heated concave depression with a microlitre syringe, a standard all-glass syringe fitted with various needles, or a dropper pipette. These gave reproducible droplets varying between 6 and 13 μl for a given hydrocarbon. These small volumes did not cool the hotplate appreciably, so the measurements were made under essentially isothermal conditions. Lifetimes were determined with an electronic stopwatch, beginning when a drop left the syringe needle. Observation through the microscope facilitated an accurate endpoint. Five drops were timed at each temperature, except around the Nukiyama and Leidenfrost temperatures where measurements on ten drops were made. The standard error of the mean lifetime was always less than 4%.

4. Results and discussion

The curve for n-octane is reproduced in figure 2, and is typical of the results obtained. The shape of the curve proved independent of droplet size over the range employed, the effect of changing volume being simply one of displacement of the entire curve along a vertical axis. The slight convexity about halfway between T_B and T_N is not mentioned by Tamura and Tanasawa, but is not thought to be an artefact because it also appears on the curves for the other hydrocarbons. The extension of the Leidenfrost curve towards lower temperatures was
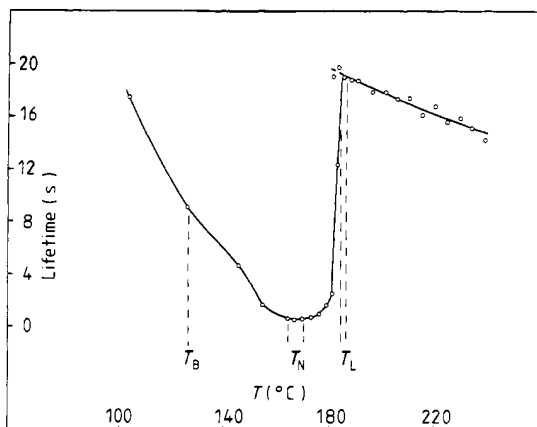
Figure 2 Drop lifetime curve for n-octane.

Table 1 The boiling point, Nukiyama and Leidenfrost temperatures (degrees centigrade) for the n-alkanes at atmospheric pressure.

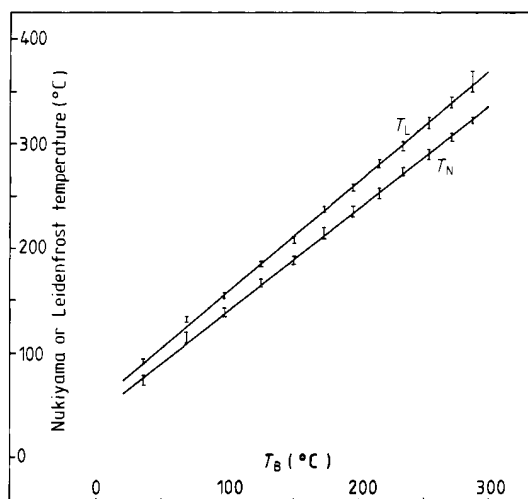| n-alkane	T_B	T_N	T_L
Pentane	36	70–78	90–93
Hexane	69	110–120	130–135
Heptane	98	135–143	152–156
Octane	126	164–170	184–186
Nonane	151	185–192	206–210
Decane	174	210–220	235–240
Undecane	195.5	230–240	255–260
Dodecane	216	248–258	278–285
Tridecane	234	270–278	294–302
Tetradecane	253.5	286–294	315–325
Pentadecane	270.5	303–309	335–345
Hexadecane	287	320–325	350–370

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

$$T_N = (0.98T_B + 42)\ °C$$
$$T_L = (1.06T_B + 52)\ °C$$

5. Possible application and extension

From our experience we can recommend this investigation as suitable for undergraduate projects, as it gives experience in searching a fair body of literature; in careful (yet comparatively simple) experimental technique; and in consideration of errors. It demonstrates some unusual facets of the phenomenon of boiling, and it will be apparent that original investigations could readily be made by extension to other organic liquids, for example the alcohols.

obtained if the droplets were pre-warmed before allowing them to fall upon the heated surface. The transitional section between T_N and T_L became less abrupt and more stable, and so easier to measure and define, as the boiling point of the liquid increased.

The broken lines in figure 2 indicate the uncertainties associated with the numerical values assigned to the Nukiyama and Leidenfrost temperatures (see table 1). It will be seen that for n-octane T_L is the better defined, but it was observed that the position tended to reverse with decreasing volatility of the hydrocarbon. This behaviour is reflected in the lengths of the error bars shown in the plots of T_B versus T_N and T_L in figure 3. The graphs are linear within the experimental error, and may be summarised by the relationships:

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